An investigation into the influences of catchment nutrient export and climatic effects on the trophic status of a small inter-drumlin lake, Milltown Lake, Co. Monaghan

By

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Abstract

Eutrophication is an on-going problem in lakes that are nutrient enriched. In addition, lakes are now subject to changes in the local weather, which is linked to climate change. Understanding the way that climate affects nutrient export and changes within lakes is critical if lakes are to be improved and protected in the future. This thesis has examined this by looking at number of different factors, which include: (1) the role of nutrients exported from the surrounding landscape and how agricultural mitigation measures (e.g. comparing a fenced stream with a vegetative buffer strips to an unfenced stream which had no fencing installed), can be used to decrease nutrient loss from the land to water, (2) examining local climatic factors and their role, either directly or indirectly, in influencing lake biota, particularly in lakes where nutrient supplies are not limiting, and finally (3) determining how phytoplankton richness is influenced by changes in water column stability during the onset of spring stratification. The study within the catchment found net retention of nutrients (TP and TN) occurred during the Grazing season (cattle grazing in the field) in the fenced stream reach, while during the Open season (slurry spreading permitted, but cattle still indoors) the reverse was seen for TP only, suggesting that different processes were controlling export of nutrients in both the fenced and unfenced reach. Despite the net TP release in the Open season, the estimated TP and TN loads on an annual basis were lower for the fenced stream, compared to that of the unfenced stream. Regarding local climatic factors, results showed that in the epilimnion of Milltown Lake, surface nutrient loading (mainly P) and light were more significant than internal lake nutrient resuspension, while N availability was more influential in controlling the standing crop of phytoplankton at the lower lake depths. In general, catchment management strategies are devised to reduce nutrient loads from the surrounding catchment in order to protect and improve catchment waterbodies, which this study has shown to be achieved through the implementation of streamside fencing with a vegetative buffer strip. However, this study has also shown that more attention is needed in understanding the internal lake sediment nutrient release, should catchment load be reduced, it is this legacy source of nutrients that is likely to play a significant role in determining a lake's trophic status.

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List of abbreviations

AEOS	Agri-Environmental Options Scheme
AIC	Akaike Information Criterion
CAP	Cattle Access Points
Chl-*a*	Chlorophyll *a*
DCM	Deep Chlorophyll Maxima
DO	Dissolved Oxygen
DS	Downstream
edf	estimated degrees of freedom
EEA	European Environment Agency
EPA	Environmental Protection Agency
EU	European Union
GAM	General Additive Model
GAP	Good Agricultural Practice
GLAS	Green Low-Carbon Agri-Environment Scheme
GLEON	Global Lakes Observatory Network
GWS	Group Water Scheme
LAWPRO	Local Authority Waters Programme
L.Flow	Log Transformed Flow
LU	Livestock Unit
NAP	National Action Programme
N	Nitrogen
N_2O	Nitrous Oxide
$NaNO_2$	Sodium Nitrite
$NaNO_3$	Sodium Nitrate
NH_4	Ammonium
NH_4Cl	Sodium Chloride
$(NH_4)_3\ PO_4$	Ammonium Phosphate
NI	Northern Ireland
NO_2	Nitrite
NO_3	Nitrate
NSPPP	National Source Protection Pilot Project
NVZ	Nitrogen Vulnerable Zone
^oC	Temperature
OSWTS	On-site wastewater treatment systems
P	Phosphorus
PAA	Priority Area for Action
PAR	Photosynthetically Active Radiation
PCA	Principal Component Analysis
PEG	Plankton Ecology Group
PO_4^{3-}	Orthophosphate
POM	Programme of Measure
RBD	River Basin District
RBMP	River Basin Management Planning
REPS	Rural Environment Protection Scheme

ROI	Republic of Ireland
S	Schmidt stability
SRP	Soluble Reactive Phosphorus
SW	Shortwave radiation
TDN	Total Dissolved Nitrogen
TN	Total Nitrogen
TP	Total Phosphorus
UK	United Kingdom
US	Upstream
USA	United States of America
WFD	Water Framework Directive
Wn	Wedderburn number

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Chapter 1: General introduction

1.1 Introduction

Cultural eutrophication is a worldwide problem which is linked to increased availability of one or more limiting growth factors needed for photosynthesis (e.g. nutrients, carbon dioxide and sunlight), and can cause a substantial increase in the density of algal cells suspended in water (Smith and Schindler 2009; Jones and Brett, 2014). Algal blooms and enhanced growth of other aquatic vegetation disrupt the normal functioning of lake ecosystems. Algal growth on the surface of lake waters limits sunlight penetration, as well as photosynthesis by the algae, causing a reduction in the oxygen levels in the lake's waters. Levels of deoxygenation are also increased by microbial decomposition of dead algae. As algae die and decompose, the levels of dead and decaying organic matter increase, in the water column and sediment, depleting the water of available oxygen and causing the death of other organisms (Capella et al., 2014). Ultimately, these limitations in available sunlight and oxygen in lakes will affect the biodiversity of a lake system, such as anoxia, development of potentially toxic blue-green algal blooms (i.e. cyanobacteria), the reduction in plant diversity, deterioration in overall water quality and fish life (Søndergaard et al., 2001; Schindler, 2006; Istvánovics, 2009; May et al., 2009; Jeppesen et al., 2012). In addition, this can have a big impact on recreational opportunities which a lake can provide (Dodds et al., 2009; Chislock et al., 2013; Hjerppe et al., 2017).

Eutrophication of freshwaters remains a recognised challenge for governments throughout the developed and developing world, particularly the control and mitigation of the impacts of nutrient transfers from land to water (Aneja et al., 2008; Vaccari, 2009; Macintosh et al., 2011). Phosphorus (P) and nitrogen (N) are the key nutrients linked to eutrophication, with excess loading increasingly being associated with agricultural practices and, to a lesser degree, point sources within Europe (Smith and Schindler, 2009; Dupas et al., 2015; EEA, 2016). In Rural areas, the point sources include on-site wastewater treatment systems (OSWTS) that service the

local population, as well as farmyards and cattle access points (CAP) to streams and lakes (Deasy et al., 2010; Neal et al., 2010; Macintosh et al., 2011). These local point sources within agricultural catchments can contribute to the overall nutrient loss, however, it is generally considered that wider, hydrology-driven diffuse sources are predominantly linked to incidental losses of nutrient stores from soils to waterbodies within these catchments (Withers et al., 2001; Jordan et al., 2005; Sharpley et al., 2013).

Throughout Europe, diffuse agricultural pollution remains an issue, regardless of improvements in the control of point sources implemented in recent decades (Smith et al., 2005; Schindler, 2006; Ulén et al., 2007; Heckrath et al., 2008; Schulte et al., 2010; Dupas et al., 2015). Mitigation measures contained within the Nitrates Directive (91/676/EEC) and the European Union (EU) Water Framework Directive (WFD) (2000/60/EC) are being used to curtail diffuse pollution within agricultural catchments. These measures include constraints on the timing and magnitude of P and N in organic and inorganic fertiliser applications, ensuring that the optimum P fertility is maintained and incidental P transfer during hydrological active periods is avoided (Fealy et al., 2010; Macintosh et al., 2011; Jordan et al., 2012). They also include fencing to exclude cattle access to streams (Galeone, 2000; Vidon et al., 2008; Miller et al., 2010).

In Ireland, agriculture accounts for 65% of the total land use by area with 81% of this area devoted to dairy and beef cattle production on managed grassland (CSO, 2015; Department of Agriculture, Food and the Marine, 2016). The total number of cattle in the Republic of Ireland (ROI) at the end of 2017 was 6,673,600 (80% beef and 20% dairy cattle), compared to an overall human population of 4,749,153 (CSO, 2018). Agriculture in Ireland mainly comprises of grassland agriculture with some 80-90% of the diet of dairy and beef animals being attributed to grass or silage that is grown on the farm (Department of Agriculture, Food and the Marine, 2016). Annual TP and TN excretion rates for cattle is 13 kg TP yr^{-1} and 65 kg TN yr^{-1} respectively, while dairy cows are estimated to be 10 kg TP yr^{-1} and 85 kg TN yr^{-1} (Ulén et al.,

2007; Stoate et al., 2009; Lewis et al., 2013; S.I. No. 31 of 2014). Spreading of slurry is prohibited during a set period in Ireland to comply with the Nitrates Directive (91/676/EEC) and depending on where in the country you live, the open dates for land spreading are from January to September and usually the closed period is October to January (Teagasc, 2011).

Problems related to eutrophication have resulted in a large body of research on both the export of nutrients to lakes (Bosch et al., 2014; Soranno et al., 2015; Vystavna et al., 2017) and possible mitigation measures (Cherry et al., 2008; Ranalli and Macalady, 2010; Miller et al., 2011). In addition, there is a substantial body of literature concerning the relationships between phytoplankton in lakes and nutrients (Hayes et al., 2015; Søndergaard et al., 2017). With lakes being under additional pressures from the effects of climate change, both past and present (Bosch et al., 2014; Hayes et al., 2015; Verma et al., 2015; Wang et al., 2018), it is important to gain an understanding of how changes in climate will affect nutrient export (e.g. during increased and more persistent rainfall events) and responses in lakes during critical times in order for lakes to be adequately managed in the future.

External nutrient sources from the wider catchment area have been the main focus of management in eutrophic lakes. However, contributions from internal lake nutrient sources, such as from lake sediments to the overlying waters, are being increasingly examined (Søndergaard et al., 2007), with a renewed emphasis on what is described as 'legacy P' (Sharpley et al., 2013). Legacy P refers to the accumulation of P in sediments found in down slope areas such as rivers and lakes which can be remobilised or recycled, thus acting as a continuing source of P to downstream waterbodies for years, decades, or even centuries (McDowell et al., 2002; Kleinman et al., 2011; Sharpley et al., 2013). In lakes, internal nutrient loading is related to high concentrations of organic P and N building up in lake sediments which is being released back into the overlying water, usually under low dissolved oxygen (DO)

conditions (Søndergaard et al., 1999; Burger et al., 2008). These nutrients can promote algal growth and impair water quality, significantly delaying remedial efforts on eutrophic lakes, even following load reduction (Meals et al., 2010; Spears et al., 2012; Sun Loh et al., 2013; Zhu et al., 2013; Wu et al., 2014; Zamparas and Zacharias, 2014).

In addition to the key role that excess nutrients play in eutrophication, it is recognised that changes in local weather conditions may also cause qualitative and quantitative changes in phytoplankton community dynamics (Paerl and Fulton, 2006; Stella et al., 2007; James et al., 2009; Cai et al., 2012). Such weather related effects are now receiving closer attention due to the long term trends attributed to climate change. Increasing water temperatures are having a direct effect on algal growth, for example, with harmful phytoplankton groups such as cyanobacteria being promoted by rising water temperatures (O'Neil et al., 2012; Deng et al., 2014; Rigosi et al., 2014). Furthermore, increases in rainfall are leading to more frequent and larger pulses of nutrient runoff from surrounding land, intensifying the symptoms of eutrophication in many freshwater lakes particularly in agricultural catchments (Jeppesen et al., 2009; Moss et al., 2011; Deng et al., 2014).

In Ireland, small lakes are prevalent, particularly in the drumlin belt, which traverses the island from County Down in the east, to Counties Sligo and Donegal on the Atlantic coast (Aalen et al., 1997; Carson, 2010). These lakes interlinked through a network of rivers and streams, and are typically small in area, with short retention times, and often serve as local drinking water sources for the surrounding communities (National Federation of Group Water Schemes, 2016). Much research has been carried out internationally that highlights the various issues affecting small, and very shallow, freshwater lakes. Previous studies by Krovang et al. (2005) and Søndergaard et al. (1999) carried out in Denmark have highlighted the delays in lake recovery following the reduction of external catchment nutrient loads, due to re-suspension of internal

nutrients from the lake sediment. Jeppesen et al. (2014) highlighted that climate change may have both direct and indirect effects on the plankton community structure. These studies highlight the complexity involved in implementing remediation measures that are required to tackle eutrophication problems in freshwater lakes.

Despite the large body of literature on nutrient mitigation measures, these studies have tended to focus on systems in the USA, Canada and Australia (McKergow et al., 2003; Galeone, 2006; Vidon et al., 2008; Bartley et al., 2010; Miller at al., 2010; Vidon et al., 2010; Miller at al., 2011), with few that relate to livestock agriculture in western Europe (Conroy et al., 2016; Bragina et al., 2017). In addition, while there is a large body of literature on small shallow lakes from mainland Europe, particularly Denmark (Trolle et al., 2015; Gutierrez et al., 2016; Søndergaard et al., 2017; Molina-Navarro et al., 2017), those lakes tend to be more shallow than Irish inter-drumlin lakes. They, therefore, tend to be more polymictic (Søndergaard et al., 2017) and more affected by sediment nutrient release (Kragh et al., 2017). There have been few studies to date on the combined effects of nutrients and weather on inter-drumlin lakes. The current study includes assessing the effectiveness of streamside fencing as a mitigation measure to reduce nutrient load from the catchment, and both internal nutrient sources and local climatic pressures, to gain an overall insight into how future catchment management strategies can be implicated for shallow drumlin lakes.

1.2 Aims and objectives

The overall aim of this study was to explore the relative effects of nutrient export from a cattle based agricultural catchment and local weather conditions as drivers of change in phytoplankton species in a small inter-drumlin lake, and therefore, to inform future management of these systems with an aim of achieving a minimum of good ecological status as set out in the WFD.

Specific objectives included:

- **Chapter 4:** Investigating the effects of agricultural management of extensive livestock farms on P and N levels in catchment streams, including the effect of excluding cattle from stream waters, using fencing as a mitigation measure.
- **Chapter 5:** Investigating the relative importance of (1.) local weather changes and their effects on lake physical characteristics, including stratification, and (2.) nutrient (P and N) levels on the standing stock of phytoplankton biomass as measured by Chlorophyll *a* (Chl-*a*).
- **Chapter 6:** Studying the relative importance of changes in water column stability, nutrient availability, and zooplankton grazing in determining plankton diversity in a small lake at the surface, and at the photic depth, during the onset of spring thermal stratification.

1.3 Knowledge gaps

- The exact timings and quantity of slurry and fertilisers application within the catchment during this study were not exactly known. This information would be difficult to obtain and require more resources. However, this information would be beneficial if a similar study were to be carried out in the future.
- There are no arterial drainage schemes within the catchment, however, the history of land improvement works carried out by farmers within the catchment is not known. Although this information is not known, an extensive stream walk of both the fenced and unfenced tributaries was carried out with no potential problematic drains identified.
- The installation of a photosynthetically active radiation (PAR) sensor within the lake and a remote weather station were not feasible for this study due to budget constraints. However, due to the proximity of two Met Éireann weather stations one in Ballyhaise, Co. Cavan and the second in Coose, Castleblayney, Co Monaghan, it is believed that the data obtained at both stations would still be sufficient in answering the questions asked in this study.

1.4 Thesis structure

The thesis is presented in seven chapters. Chapter one provides the study background and detailed description of the study objectives. A detailed literature review is presented in Chapter two, focusing on the role that climate and nutrients (P and N) play in controlling phytoplankton biomass. Chapter three describes the location of Milltown Lake and its catchment, along with the general material and methods used during this research. Chapter four presents the results of a study which focused on the effects of streamside fencing within the Milltown Lake Catchment and its ability to reduce nutrient loss to surface water . This was assessed by comparing a fenced and an unfenced tributary stream reach with similar topography and land management practices during three contrasting management periods in the Irish agricultural calendar. Chapter five looks at the long-term thermal structure in Milltown Lake using high frequency weather and *in-situ* temperature sensor data between April 2010 and September 2012. This chapter then particularly focuses on the importance of climate and nutrients as drivers in controlling the standing stock of phytoplankton biomass as measured by Chl-*a* during the growing season in 2012. Chapter six further investigates the influence that thermal dynamics play in plankton structure during the onset of stratification. This was assessed by looking at the physical parameters, nutrient concentrations, and plankton communities during the spring of 2013. Chapters four to six each contain an abstract, detailed introduction, methods, results, discussion and conclusion sections. Chapter seven discusses the findings of the previous chapters, presenting the final conclusions and highlighting the potential application of this research to other eutrophic lakes and catchments.

1.5 Hypotheses

- **Chapter 4:** Streamside fencing and thus cattle exclusion will reduce the overall P and N concentrations in streams within agricultural catchments.

- **Chapter 5:** Local climatic factors (wind and rainfall), physical drivers (thermal stratification) and nutrient (P and N) concentrations does influence phytoplankton biomass within a small lake.
- **Chapter 6:** Water column stability, nutrient (P and N) availability and zooplankton grazing are drivers in determining plankton diversity at both the subsurface and photic zone depth during the onset of spring thermal stratification.

Chapter 2: Literature review

2.1 Sources of phosphorus and nitrogen in lakes

Although natural eutrophication is a slow-aging process for a waterbody, human activities speed up the process greatly (Art, 1993). Within a lake's catchment, it is geology and land use that generally determine the amount of nutrients entering the lake either *via* surface water or groundwater channels. Water transported by the rivers and streams draining into a lake carry with them much of the suspended sediment and nutrients which have runoff from the surrounding landscape. When river water enters a lake, its speed diminishes rapidly, bed-load transport ceases, and the suspended load of sediments and nutrients begins to settle to the bottom. However, external nutrient loads from the surrounding catchment are not the only sources of elevated nutrient concentrations in lakes. Internal lake sediment can play an important role in the retention and release of nutrients depending on lake depth, due to physical (wind, temperature and stream discharge), chemical (oxygen depletion in the hypolimnion, resulting in nutrient release from the lake sediment due to anoxia) and biological factors (decomposition of organic matter) (Egemose et al., 2011; Palmer-Felgate et al., 2011; Søndergaard et al., 2013).

2.1.1 Phosphorus loss from surrounding agricultural land

Phosphorus losses from land are mainly associated with the erosion of P enriched soils, especially from bare or poached soils, with excess manure/fertiliser applications and with surface runoff of dissolved forms occurring during heavy rainfall (Haygrath and Jarvis, 1999; Hooda et al., 2000; Jennings et al., 2003; Kiely et al., 2007; Palmer-Felgate et al., 2009; Macintosh et al., 2011). Concentrations of P in runoff, particularly from agricultural land, are dependent on the quantities of P present in, or on, the soil and the extent to which water moving through or over the soil captures these sources (Jennings et al., 2003; Withers and Hodgkinson, 2009). The form of P transported in runoff from organic fertiliser spreading on grassland is

variable, depending on specific farming practices. Organic P is the principal form of P in slurry and animal manures, comprising approximately two-thirds of the P in fresh manure (Jordan and Rippey, 2003; Kurtz et al., 2005; Withers and Hodgkinson, 2009). In contrast, inorganic P is the main component of chemical fertilisers (Dils et al., 1999) and can be found in either soluble or bound forms.

Soluble inorganic P is a strong anion that is highly reactive and, therefore, attaches to exchange sites in the soil (Daly et al., 2002). This is the form of P that is taken up by plants (Cordell et al., 2009) (Figure 2.1). Over time, soluble inorganic P will react with cations such as calcium, iron, aluminium and manganese, slowly converting to a less soluble form known as unavailable inorganic (bound) P (Figure 2.1). This limits its availability to plants (Wiederholt and Johnson, 2005). A large fraction of soil P exists as bound inorganic P and can either be attached loosely or tightly to cations. Loosely bound P particles can remain in equilibrium with soluble P and become available in soil pore waters (Figure 2.1). This enables bound inorganic P to be converted into soluble inorganic P when plant removal reduces the concentration of soluble P, thus maintaining the equilibrium (Wiederholt and Johnson, 2005).

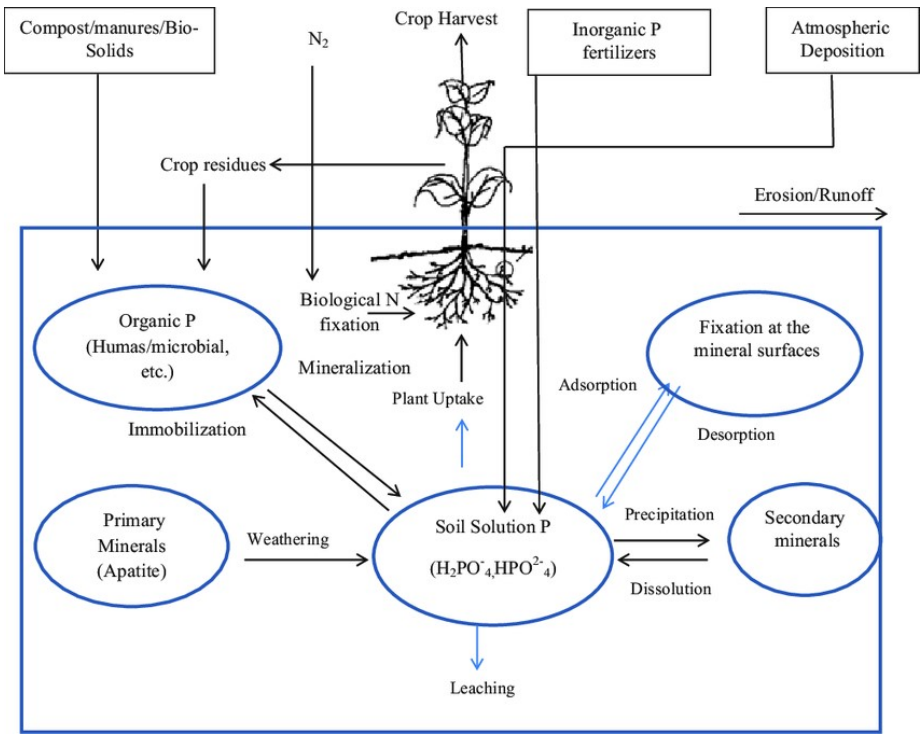

Figure 2.1 Phosphorus Cycle (Kumar et al., 2018).

The export of nutrient in overland flow related to fertilisers and manures is more prevalent after periods of heavy rainfall, with areas of land that have a high soil test P being the more susceptible (Galeone, 2006; Reichenberger et al., 2007; Buckley, 2012). Soil erosion by water includes the processes of detachment, transportation and deposition of the soil particles by raindrops or surface flow (Foster et al., 1985; Hatfield and Follett, 2008). High rainfall events can be associated with higher losses of particulate P and dissolved P. However, particulate material will only be transported during high rainfall events (Macintosh et al., 2011). In some agricultural areas, artificial land drains can represent an important pathway of particulate P, particularly during periods of heavy rainfall, as they tend to have a direct pathway to the watercourse (Chapman et al., 2001; Jennings et al., 2003; Montagne et al., 2009; Vidon et al., 2012). A further source of particulate P loss from agricultural land is through increased animal activities around and within streams, resulting in bankside erosion of soil and disturbances of the streambed sediment (Clew et al., 2010; Bond, 2012).

In Ireland, incidental P transfers from slurry and manure management, fertiliser spreading, and diffuse losses from high nutrient status soils all contribute substantially to agricultural P losses (Schulte et al., 2010). In European countries such as Norway and Sweden, where arable agriculture predominates and plant cover may be absent for long periods, sediment P losses to water are a particular problem (Ulén et al., 2007). A summary of TP exports in small agricultural streams reported in studies carried out in Northern Europe and Ireland is summarised in Table 2.1.

Table 2.1 Summary of TP exports in small agricultural streams in Northern Europe.

Study	Export (kg TP ha^{-1} yr^{-1})	Description of catchments
Ulen et al. (2007) & Stoate et al. (2009)	0.3 – 6.0	Estimation of TP export in north-western European countries (Norway, Sweden, Ireland and the UK), with the highest losses in Norway and UK.
Jordan et al. (2007)	0.2 – 3.1	Three different grassland catchments in Ireland.
Green et al. (2001)	0.1 – 1.0	Lough Sheelin a drumlin grassland catchment in central Northern Ireland.
Macintosh et al. (2011) & Cassidy and Jordan (2011)	1.8 – 3.8	Cross border grassland catchment in between Northern Ireland and Ireland over a four year study period.
Jennings et al. (2013)	0.55	Lough Leane, a large lake with both agriculture and peatland sub catchment in Co. Kerry, Ireland.
Mellander et al. (2012)	0.54 – 0.70	Four agricultural catchments (arable and grassland) across Ireland.

2.1.2 Nitrogen loss from surrounding agricultural land

Nitrogen losses to waterways are mainly attributed to over-fertilisation, excessive manure applications, autumn ploughing, intensive stocking of pastures, cattle access to waterways and mineralisation of soil organic material (Shepherd et al., 2001; Follett, 2008; Zaied, 2009). The predominant forms of N in the soil are ammonium (NH_4^+) and nitrate (NO_3^-), with nitrite (NO_2^-) and nitrous oxide (N_2O) being present to a lesser extent (Dalgaard et al., 2011) (Figure 2.2). Nitrogen is required for the survival of all living things and is an essential nutrient for the production of crop plants (Follett, 2008). Plants tend to take up N as NH_4^+ and NO_3^-, whereas NO_2 is essentially toxic to plants (Taylor and Klepper, 1975). The main processes in the nitrogen cycle involve nitrogen fixation, ammonification, nitrification and denitrification (Figure 2.2). The initial process nitrogen fixation is where N_2 is transformed to organic nitrogen in order for the consumption by living organisms (Figure 2.2). This process is considered the most dominant process by which N enters the soils biological pool (Robertson and Groffman, 2007). Once N has entered the soil or water, it undergoes the process of ammonification whereby bacteria convert N or nitrogen compounds into NH_4^+. Ammonium, with its positive charge, bonds to the negatively charged surfaces of soil particles and has a strong affinity to

clay in particular (Seybold, 1994). Soil concentrations are generally quite low, because the biological conversions from NH_4^+ to NO_3^-, which are favourable for mineralisation, tend to be rapid (Brown, 1993). Nitrite is an intermediate species in the conversion from NH_4^+ to NO_3^- and tends not to accumulate in soil because the conversion from NO_2^- to NO_3^- is much faster than from NH_4^+ to NO_2^- (Burns et al., 1996) (Figure 2.2). Nitrate is a weak anion and a very soluble compound; therefore, it does not have a strong affinity to bind to the soil or to other insoluble compounds present in the soil (Krammer et al., 2006).

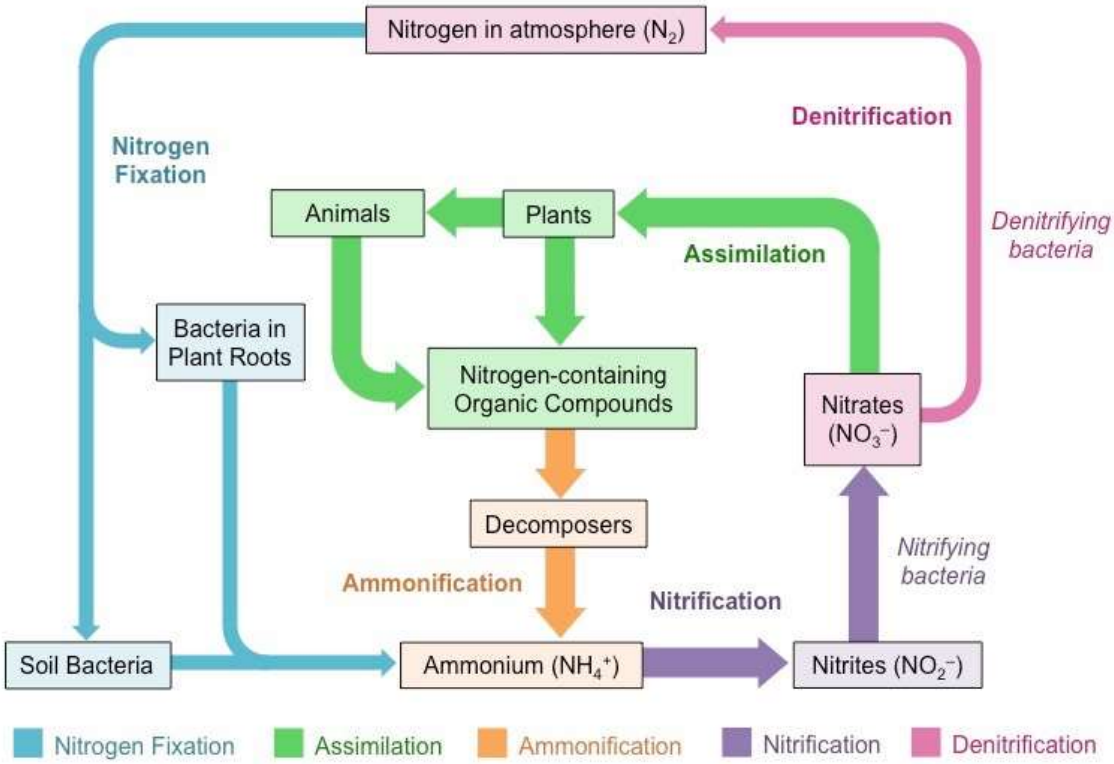

Figure 2.2 Nitrogen Cycle (ib.bioninja.com.au, 2016).

Nitrogen is typically leached from a surface source to groundwater as NO_3^- and usually reaches surface waters via subsurface groundwater channels or artificial drains (Kc, 2007; Robertson and Vitousek, 2009; Follet et al., 2010; Mellander et al., 2012). Elevated N in groundwater often results in poor drinking water quality, with concentrations reaching levels above those acceptable for drinking water supply (i.e. < 50 mg NO_3 L^{-1}) (Directive 91/676/EEC). Losses of N may, however, also occur via surface runoff (Jiao et al., 2006). Surface runoff occurs when rainfall exceeds the maximum infiltration level of the soil (Heathwaite et al., 1998). Movement

of N into surface water from soils is mainly associated with soil erosion during heavy rainfall and, to a lesser degree, through wind deposition (Cameron and Haynes, 1986). Some sediment particles may travel only a few millimetres, while others may be transported long distances before they are deposited or reach a surface water receptor (Follet et al., 2010). Nitrogen is primarily transported as organic N in soil or sediment organic matter, or as NO_3^-, a form that is completely water soluble (Follet et al., 2010; Yang et al., 2013). However, agricultural soils that have recently received fertiliser and manure applications containing high NH_4^+ concentrations can result in NH_4^+ being washed from the land to nearby surface waters following episodes of high rainfall (Burns et al., 1996).

In the 2010 agricultural census, cattle density in Ireland had increased from the 0.76 livestock units (LU) ha^{-1} reported in 1970 to 1.54 LU ha^{-1} (CS0, 2010). Animals, in particular cattle, defecate on the fields and, in some cases directly into watercourses where access is permitted (Bond et al., 2012). High densities of dung and increased levels of soil-profile NO_3^- are frequently observed in areas near watering and shade points (Wilkinson et al., 1989; Haynes and Williams, 1993; Follett, 2008). The levels of nutrients, especially NH_4^+, associated with fresh animal faeces or urine increase immediately in stream waters when in-stream livestock activity occurs (Demal, 1983; Sheffield et al., 1997; Miller et al., 2011).

In Europe, N from mineral fertilisers is the more dominant source of N, with animal manure, particularly chicken manure, being prominent in regions with high stocking density (McKauge et al., 2005). There are large differences in total nitrogen (TN) input, output and surplus for agricultural land between countries (Velthof et al., 2009). A summary of TN exports in small agricultural streams reported in studies carried out in Northern Europe and Ireland is summarised in Table 2.2.

Table 2.2 Summary of TN exports in small agricultural streams in Northern Europe.

Study	Export (kg TN ha^{-1} yr^{-1})	Description of catchments
Velthoh et al. (2009) & EEA (2010)	<50	Central Europe (Bulgaria, Estonia, Latvia and Romania)
	170	Denmark, Belgium and the Netherlands
Venhor et al. (2005)	10.8	Lough Mask Catchment spanning between Co. Mayo and Co. Galway, Ireland.
Fealy et al. (2010) & Wall et al. (2011)	8.9 – 28.8	Six agricultural catchments (arable and grassland) across Ireland
Jordan and Smith (2005)	24.4 & 13.3	Grassland and unimproved grassland catchments in the sub-catchments of the River Upper Bann and the River Colebrooke

2.1.3 Internal nutrient loading from phosphorus and nitrogen to lakes

Internal cycling of nutrients is an important factor that supports to plankton productivity (Gardner et al., 1998), with lake sediments being an important source, particularly in freshwater lakes (Zhu et al., 2012). Phosphorus plays a key role in lake ecosystems, having a longer residence time and higher retention efficiency than N (Saunders and Kalff, 2001; Jeppesen et al., 2005; Cook et al., 2010; Grantz et al., 2014; Yan et al., 2016). Recently, however, besides the role of P, the importance of N limitation for lake productivity has been more intensively studied and discussed (Sterner, 2008; Conley et al., 2009; Moss et al., 2013; Olsen et al., 2015a; Søndergaard et al., 2017).

Phosphorus, once introduced into a lake's ecosystem, accumulates in the bottom sediments, which are considered net sinks and tend to have higher P concentrations than the overlying waters (Wetzel, 2001). Sedimentary P can act as a large internal load to the overlying water column, contributing to the growth of algal blooms, impairing water quality and significantly delaying remedial efforts in eutrophic lakes, even following external load reduction (Sun Loh et al., 2013; Zhu et al., 2013; Wu et al., 2014). The release of sedimentary P is influenced by various environmental factors, including temperature, pH, redox potential, DO, hydrological

conditions and biological activity (Kleeberg et al., 1998; Miao et al., 2006; Wu et al., 2014). The main P fraction released from the sediment is highly biologically available orthophosphate (unbound PO_4^{3-}). This form of P, when released during the period of thermal stratification of a monomictic or dimictic lake, can contribute to an increase in phytoplankton biomass during the summer and autumn months (Nürnberg, 2009; Sun Loh et al., 2013). Internal P loading during the winter can also increase spring productivity unless limited by light (Sun Loh et al., 2013). Studies have shown that sedimentary P release is mainly from the surface layer of the benthic sediment, therefore, the potential influence of sediment P in shallow lakes on water concentrations is stronger than that of deeper lakes, due to the ability for wind to mix up the benthic sediment in shallower lake systems (Søndergaard et al., 2003).

The N cycle is a complex biochemical process in which the various forms of N are altered by N fixation, assimilation and reduction of NO_3 to N_2 by denitrification (Wetzel, 2001). Wetzel (2001) described the simplified N cycle of lakes to be microbial in nature, with bacterial oxidation and reduction of N compounds being coupled with photosynthetic assimilation and utilisation by algae, photosynthetic bacteria and larger aquatic plants. In freshwater lake ecosystems, NH_4 can stimulate phytoplankton growth, exhibit toxicity to aquatic biota, and exert an oxygen demand on the surface waters (Beutel, 2006). In productive lakes, NH_4 concentrations accumulate from decomposition of organic matter and sediment release of NH_4 to the overlying waters can occur under anoxic conditions (Wetzel, 2001). Increases in N concentrations can negatively affect and degrade the ecological quality of a lake in several ways, for example by contributing to an increase in cyanobacterial biomass and dominance (Xu et al., 2010; Jeppesen et al., 2011; Davis et al., 2015). In some shallow lakes, the growth and species diversity of submerged macrophytes has been shown to be negatively impacted due to enhanced shading by phytoplankton and/or periphyton or effects of toxic stress on plant metabolism (Barker et al., 2008; Yu et al., 2015; Olsen et al., 2015b; Søndergaard et al., 2017).

For instance, Olsen et al. (2015) showed, in a controlled experiment carried out on Lake Donghu (surface area 32 km^2, mean water depth 2.5 m) how the macrophyte population is partially resilient to abrupt increases in N loading, but, after prolonged exposure, a complete collapse occurs. Furthermore, Olsen et al. (2015) showed that macrophyte loss is intensified by the shading of filamentous algae during the winter months and by phytoplankton in the summer months.

2.2 Stratification of lakes

Thermal stratification is a natural phenomenon that occurs in lakes as a result of the thermal expansion properties of water (Read et al., 2011; Woolway et al., 2017). It is determined by the balance between turbulence, which acts to enhance mixing, and buoyancy forces, which act to suppress turbulence, resulting in vertical layering (Boehrer and Schultze, 2008; Woolway et al., 2014). The epilimnion is defined as that part of the water column that is immediately below the water surface, and directly influenced by atmospheric forcing, while the hypolimnion, generally the coolest and thus the densest layer, lies in contact with the lakebed. Both of these layers are separated by a temperature-driven density gradient known as the thermocline (Woolway et al., 2017). This vertical partitioning of the water column has important implications for the transport of nutrients and oxygen between the surface and deep water, or the light environment experienced by phytoplankton cells entrained in the mixed layer (Foley et al., 2012; Kirillin and Shatwell, 2016).

Stratification can be temporary or persistent, and its duration can vary from hours to months or even decades in some lakes (Jellison et al., 1998; Verburg et al., 2003; Rueda and Schladow, 2009). Shallow lakes, which mix to the bottom regularly, behave quite differently to deeper lakes, which tend to stratify as the weather warms causing a warmer, well-mixed layer to develop above a cooler poorly mixed layer, separating the surface water from deep, nutrient

rich waters and sediment (Kirillin and Shatwell, 2016). Shallow lakes, which do not develop a full seasonal stratification but tend to alternate between periods of mixing and stratification, tend to be strongly driven by meteorological conditions (Woolway et al., 2014; Woolway et al., 2017). These lakes are often termed polymictic according to Hutchinson's mixing classification and tend to be most abundant at mid-latitudes (Hutchinson, 1957; Woolway et al., 2017). In contrast, lakes that stratify continuously for a large part of the year are classified as dimictic (stratification in the summer and inverse stratification in winter), or monomictic if they stratify only once a year, either in the summer or winter months (Hutchinson and Löffler, 1956; Hutchinson, 1957; Lewis, 1983; Kirillin and Shatwell, 2016).

The main external stressors determining the mixing regime of lakes are meteorological conditions, changes in inflow discharge, and differences in lake morphology (Fee et al., 1996; Rimmer et al., 2011). Wind stresses that occur at critical time windows can result in the interruption or even breakdown of thermal stratification (Adrian et al., 2012; Jennings et al., 2012; Sommer et al., 2012). In addition, water transparency, or light extinction also play a major role in determining the mixing regime between polymictic and seasonally stratified lakes (Snucins and Gunn, 2000; Kirillin, 2010; Shatwell et al., 2016). For instance, transparency reduces the penetration of solar radiation to deeper layers, decreasing water temperatures and increasing vertical temperature gradients and water column stability (Kirillin and Shatwell, 2016).

Traditionally, lake depth temperature measurements have typically been collected on a weekly or fortnightly basis, although high-frequency monitoring of surface temperatures have been made (Maberly, 1996; Livingstone and Kernan, 2009). However, with the development of automatic in lake aquatic depth sensor technology, a large volume of data is rapidly being accumulated for lakes across the world (Porter et al., 2009; Read et al., 2011). This has allowed

the frequent monitoring of lake vertical temperature profiles from in-situ lake sensor platforms. To process such information more easily, the Lake Analyzer programme was created for the analysis of high-frequency data collected from instrumented lake buoys (Read et al., 2011).

2.3 The effects of wind on the breakdown of thermal stratification

The effect of wind stresses on a lake ecosystem is generally not associated with any seasonal or annual pattern. However, increased wind speeds can interrupt or even break down thermal stratification during a crucial time for a lake's ecosystem (Adrian et al., 2012; Jennings et al., 2012; Sommer et al., 2012). Moreno-Osten et al. (2009) showed that phytoplankton in the epilimnion responded rapidly to wind stresses in a Spanish lake. Wind induced mixing facilitates internal nutrient mixing, helps phytoplankton species to remain in suspension, facilitates species replacement and transports deeper species into the upper water column, therefore, changing the competitive balance between species (Huisman et al., 2004). Monero-Osten et al. (2009) studied the impact of short-term wind induced mixing on phytoplankton, specifically diatoms (negatively buoyant) and cyanobacteria (positively buoyant) and found that a higher biomass of diatoms occurred in the upper epilimnion in the winter during higher wind speeds, while a decline was evident in diatom concentrations during lower wind speeds. Regarding cyanobacterial behaviour, higher biomass in the upper epilimnion followed periods of lower windspeed, while lower biomass in the epilimnion occurred with increasing wind speeds. Huisman et al. (2004) reported similar findings with buoyant phytoplankton species, such as cyanobacteria, dominating in low turbulence conditions in a hypertrophic lake in the Netherlands, while sinking diatoms and green algae dominated in high turbulence conditions. Ibelings et al. (1994) suggested that lake stability is important for the formation of cyanobacteria blooms and that mixed conditions in lakes, associated with high wind speeds, inhibit the formation of cyanobacterial blooms.

2.4 Effects of light on phytoplankton groups

Phytoplankton are photoautotrophic, capturing and using solar energy in photosynthesis (Wetzel, 2001; Reynolds, 2006; Litchman and Klasmeijer, 2008). Phytoplankton must cope with a wide range of incident irradiance (Suggett and Borowitzka, 2010). Even without the fluctuation due to clouds, surface wave focusing or vertical mixing, phytoplankton need to remain in the upper layers of the water column for survival, where they have adapted to diel changes in light intensities (Reynolds, 2006; Suggett and Borowitzka, 2010). Three processes allow phytoplankton to adapt to changing light regimes, which all work at different time scales: adaption, acclimation and regulation (Huot and Bain, 2010). Due to changes in the genetic make-up of phytoplankton, different species are best suited for growth in different light environments, known as photoadaptation (Suggett and Borowitzka, 2010). Photoacclimation is when phytoplankton adjust their capacity to harvest and utilise light (e.g. add and remove pigments) to maintain photosynthetic efficiency under a variety of light intensities due to a change in environmental conditions (Geider et al., 2009). Finally, when phytoplankton cells respond to rapid changes in light intensity on a diel scale, and also accommodate changes in cloud cover, this is known as photoregulation (Huot and Bain, 2010). Photoregulation strategies of phytoplankton can reduce the capacity of photosynthesis to avoid cell damage at high light intensities, normally occurring under calm low wind conditions. The recovery from photoinhibition activities can occur within hours (Hiriart-Baer and Smith, 2005). Phytoplankton at the surface of lakes that are exposed to high UV-light can result in damage to the photosynthetic pigments and DNA of the plankton cells. To overcome this, cells exposed to high light irradiance generally have a lower content of Chl-*a* per cell in comparison to phytoplankton adapted to lower irradiance levels (Wetzel, 2001).

2.5 Effects of nutrients on phytoplankton groups

The controls on the community structure of phytoplankton have been the subject of intense study for many decades (Lynch and Shapiro, 1981; McQueen et al., 1989; Agawin et al., 2000;

Irwin et al., 2006; Zhu et al., 2010; Winder and Sommer, 2012; Deng et al., 2014; Carey et al., 2017). Generally, increased nutrient loads are thought to drive increases in cyanobacterial blooms in freshwater lakes (Brookes and Carey, 2011). However, under excessive nutrient loading conditions, a shift from cyanobacteria to chlorophytes has also been reported by Jensen et al. (1994), who studied approximately 200 shallow Danish lakes with a mean depth of < 3 m. This shift is largely due to the high growth and loss rates and, thus, higher demand for nutrients by chlorophytes in temperate lakes, whereas cyanobacteria have lower growth and loss rates and a lower demand for nutrients (Reynolds, 1984; Deng et al., 2014).

Seasonal variation in nutrient availability plays an important role in driving the change in phytoplankton community structure during different periods, with certain nutrients being limiting in the spring and different nutrients dominating the nutrient limitation process in the summer (Moss et al., 2013). For instance, during spring, increased losses from the catchment to the lakes, due to agricultural practices, can provide an excess loss of N over P. Therefore, as growth ends, P will have become depleted, while N will still be available (Lund, 1967; Moss et al., 2013). However, as lake water temperatures increase, resulting in stratification and deoxygenation of the hypolimnion, or as the sediments in a shallow lake become warmer and bacterial activity intensifies, releases of sediment P tends to increase, whilst N tends to denitrify as the water warms (Moss et al., 2013). This is particularly apparent in small shallow eutrophic lakes, as shown by Søndergaard et al. (2005), who found that, as P increased in the overlying water, a depletion of N occurred during the summer months, a process that may encourage the growth of N fixing cyanobacteria.

2.6 Chlorophyll *a* as a proxy for phytoplankton biomass

The measurement of phytoplankton biomass is a fundamental part of limnological assessments, although direct measurements are difficult. It is generally estimated either from cell counts or

from the concentration of the photosynthetic pigment Chl-*a* (Billington, 1991; Wetzel, 2001). Historically, measurements of Chl-*a* have, provided a useful estimate of algal biomass and its spatial and temporal variability. The pigment is present in all species of phytoplankton, including eukaryotic (algae) and prokaryotic organisms (cyanobacteria) (Gregor and Maršálek, 2004). The concentration of Chl-*a* present in a water sample is usually directly related to the number of algae living in the lake, therefore, acting as an indicator of the trophic state of a waterbody, with high levels indicating eutrophication. Chlorophyll *a* concentration is relatively easy and rapid to quantify, thus making it a reliable and popular proxy for total phytoplankton biomass (Felip and Catalan, 2000). Measurements are carried out by extracting the Chl-*a* pigment and quantifying the concentrations present using a spectrophotometer (Marra, 1997; Felip and Catalan, 2000; Mignot et al., 2011). Alternatively, Chl-*a* fluorescence can be used (Marra, 1997; Mignot et al., 2011).

Of the methods used to measure phytoplankton biomass there are different difficulties associated with each. The counting of phytoplankton cells can be time consuming and requires consistency to reduce errors associated with biomass calculations (Beardall et al., 2009). Additionally, the time required to count the cells, generally mean that the data obtained are at low resolution. With Chl-*a* extraction methods, all samples are measured at a specific wavelength which does not differentiate among the different phytoplankton species. In addition, Chl-*a* fluorescence measurements are also not a perfect proxy either, due to problems associated with converting the fluorescence signal into an accurate Chl-*a* concentration and issues relating to fluorescence quenching (Marra, 1997; Mignot et al., 2011).

2.7 Combined effects of climate and nutrients on phytoplankton biomass

It has long been recognised that combinations of nutrients (P and N) play an important role in the amplification of algal blooms in lakes (Paerl and Fulton, 2006; James et al., 2009; Cai et

al., 2012). This has been illustrated by various modelling studies (Elliott, 2005; Markensten et al., 2010), historical data analyses (Wagner and Adrian, 2009; Stich and Brinker, 2010) and experimental studies (Moss et al., 2003; McKee et al., 2003). However, it is also apparent that changes in local weather may also cause qualitative changes in phytoplankton community dynamics, with water temperatures playing a direct role in influencing algal growth (Stella et al., 2007). For instance, harmful algal blooms react positively to rising water temperatures (Paerl and Huisman, 2008; Cai et al., 2012; Deng et al., 2014). Many studies have reported that rising temperatures enhance cyanobacterial biomass compared to other phytoplankton species, such as diatoms and green algae (O'Neil et al., 2012; Deng et al., 2014; Rigosi et al., 2014). In addition to rising air temperatures, other aspects such as water temperatures increasing due to light absorption by algal blooms and increases in rainfall leading to nutrient runoff from surrounding catchments, also intensify symptoms of eutrophication in many freshwater lakes (Jeppesen et al., 2009; Moss et al., 2010; Deng et al., 2014).

2.8 Policy and management

In December 2000, the publication of the EU WFD (2000/60/EC) marked a turning point in the perception and management of water quality in Europe, establishing a framework for improving both surface and groundwater quality (Free et al., 2016). It is an important piece of environmental legislation outlining the requirements needed to carry out water protection and water management measures, which are integrated and targeted and which initially aimed to achieve an overall objective of at least 'good status' for Irish waters by 2015 or no further deterioration by 2027 (Cherry et al., 2008). The WFD was transposed into Irish Law by the European Communities (Water Policy) Regulations 2003 (SI No. 722 of 2003) in December 2003 (Earle and Blacklocke, 2008). The WFD runs in 6 year cycles up until the end of 2027 and is being implemented through river basin management planning (RBMP) which includes measures to address pollution from agricultural sources (WFD, 2000/60/EC). In the first six

year cycle of the RBMP which ran from 2009 and finished at the end of 2015, Ireland chose to undertake activities associated with the WFD through the creation of seven River Basin Districts (RBDs) (Earle and Blacklocke, 2008). Each RBD had individual RBMPs, which aimed to achieve the objectives of the WFD. It is acknowledged, however, that sufficient progress was not made in developing and implementing supporting measures during the first cycle of the RBMP (Department of Housing, Planning, Community and Local Government, 2018). According to the figures detailed in the RBMP for Ireland 2018 – 2021, 43% of river and 45% of lakes in the ROI did not meet their environmental objective in the first RBMP cycle (2009-2015) with 32% of rivers and lakes in Northern Ireland (NI) not achieving good ecological status (DAERA, 2018). Of those in the ROI, 53% of failures are suspected to be due to agricultural sources of pollution (Bradley et al., 2015; Deakin et al., 2016; Department of Housing, Planning, Community and Local Government, 2018). However, key measures which were implemented during the first cycle included the licensing of urban waste-water discharges (with an associated investment in urban waste-water treatment) and the implementation of the Nitrates Action Programme (Good Agricultural Practice Regulations) (Department of Housing, Planning, Community and Local Government, 2018). This current second cycle of the RBMP which is running from 2016 to the end of 2021, aims to build on the progress made and lessons learned from the first cycle (Department of Housing, Planning, Community and Local Government, 2018). Firstly, the structure of multiple RBDs did not prove effective, either in terms of developing the plans or the implementation of those plans. Secondly, the governance and delivery structures in place for the first cycle were not as effective as expected, and thirdly, the targets set for the first cycle were too ambitious and were not grounded on a sufficiently developed evidence base (Department of Housing, Planning, Community and Local Government, 2018). The current RBMP plan (2016 – 2021) has focused on combining the seven RBD's which were established in the first cycle to form a single RBD. In addition, the current RBMP has lists 190 Priority Areas for Action (PAA's), which include 726 waterbodies, where

collaborative efforts will be focussed to improve water quality, which will be assisted by the newly established Local Authority Waters Programme (LAWPRO). The LAWPRO Catchment Scientist will carry out as part of their work 'on the ground' actions and stream walks to gain a better understanding of the issues impacting on water quality in these PAA's with an aim to develop solutions that are relevant and workable locally.

In 1991, the EU introduced the Nitrates Directive (91/676/EEC). This is a precursor of the WFD (2000/60/EC) and aims to minimise surplus P and N losses from agricultural practices to the aquatic environment (Buckley, 2012). The Directive requires member states to designate all areas of land which drain into surface or groundwater's where NO_3^- exceeds 50 mg N L^{-1}, where nitrogen concentrations are showing a rising trend or where evidence of eutrophication and a significant amount of N present come from agricultural sources such as Nitrate Vulnerable Zones (NVZ) (Jordan and Smith, 2005). Giving effect to the Nitrates Directive in Ireland and supported by successive national regulations, the Nitrates Action Programme (NAP) was designed to prevent pollution of surface waters and groundwater from agricultural sources and to protect and improve water quality (Buckley, 2012; S.I. No. 605 of 2017). Subjected to a four year review cycle, the NAP's are now more commonly referred to as the Good Agricultural Practice (GAP) Regulations (Buckley, 2012).

One of the main focuses covered within the GAP Regulations, is outlining the minimum slurry storage requirements for housing livestock over the winter. This then aids in facilitating a closed slurry spreading period during the autumn and winter months and prevent incidental diffuse transfer of nutrients during heavy rainfall periods (Buckley, 2012). In Ireland, the voluntary agri-environmental scheme, Rural Environmental Protection Scheme (REPS), was introduced in 1992 and had a whole-farm focus. It evolved through four iterations (REPS 1, 2, 3 and 4) (Department of Agriculture, Food and Marine, 2017). The main purpose of the scheme was to

encourage farming in an environmentally friendly manner, placing much of the emphasis on biodiversity (Emerson and Gillmor, 1999; Feehan et al., 2005; Department of Agriculture, Food and Marine, 2017). Partial fencing of waterbodies was a requirement of this scheme, although cattle access to some stream segments for drinking water purposes was permitted (Department of Agriculture, Food and Rural Development, 2000; Feehan et al., 2005, VanRensburg et al., 2009). Initial uptake of the REPS scheme was slow, however, when it closed to new applicants in 2009, more than 60,000 farms were receiving payment, which represented 45% of farms in the ROI (Finn and Ó hUallacháin, 2012). It was succeeded, in 2010, by a smaller Agri-Environment Options Scheme (AEOS), which ran for three funding cycles until the end of 2013, taking a more targeted approach by focussing on part-farm actions (Department of Agriculture, Food and Marine, 2016). The current agri-environmental scheme introduced in the ROI is called Green Low-Carbon Agri-Environment Scheme (GLAS) (2014-2020). This scheme builds on the previous schemes primarily through encouraging farmers to protect water bodies from cattle by prohibiting cattle access to the waterways by implementing streamside fencing (Department of Agriculture, Food and Marine, 2015). Agri-environmental schemes similar to those run in the ROI have been adopted throughout the EU to help achieve the aims of the WFD (Batáry et al., 2015).

Chapter 3: Site description and methods

3.1 Introduction

This chapter provides a detailed description of the Milltown Lake Catchment study site. A general overview of materials and methods is given in this chapter, with greater detail outlined where applicable in their respective subsequent chapters. Methods which are described in this chapter include (1) where stream discharge and meteorological data was obtained, (2) how nutrients (TP, TN, soluble reactive phosphorus (SRP), NO_3-N, NO_2-N, NH_4-N and TDN) were analysed, (3) the deployment of the automatic sensor in Milltown Lake and (4) how chlorophyll *a* analysis was determined.

3.2 Site description

Milltown Lake (54º8'43"N; 6º42'35"W), sometimes referred to as Muchno Mills, has an area of approximately 0.14 km^2 (Figure 3.1; Figure 3.2a). The lake is relatively shallow, with a mean depth of 5.5 m and a maximum depth of approximately 10 m and has an estimated retention time of 25 days. The lake has one main inflow, the Drumleek River, and a single outflow, the Frankford River. The Drumleek River branches into three inflowing tributaries (440 m above lake) which are not named on the Ordnance Survey maps or locally (Figure 3.1a). Two of the larger tributaries of the Drumleek River are fed by small lakes. These include a small lake on the western tributary in Carnagh Forest, Tievenamara (54°12'4"N; 6°43'49"W) which is unnamed on the Ordnance Survey maps and Gentle Owen's Lake on the middle tributary (54°12'29"N; 6°42'45"W) (Carson, 2010). The lake is used as a domestic water supply for the local communities (abstracting approximately 286, 290 m^3 per annum), which is typical of the small drumlin lakes that are found across the region. It is part of the Churchill and Oram Group Water Scheme (GWS) serving approximately 748 premises (Linnane et al., 2011). Recreational activities include angling, with the lake being stocked (rainbow trout and brown trout) on an annual basis for the local angling club.

Milltown Lake Catchment (54º8'44"N; 6º42'44"W) is situated in County Monaghan, north-central Ireland (Figure 3.1a, b). The catchment is a sub-catchment of the River Fane, which is situated in the Neagh-Bann International RBD. The total area of the catchment including Milltown Lake is 30.6 km^2. Of this approximately 8 km^2 lies within Northern Ireland, providing a North-South cross-border element to the study (Linnane et al., 2011). The lake is an inter-drumlin lake and is located in the drumlin belt of Ireland, which stretches from Strangford Lough in County Down to Clew Bay in County Mayo. The drumlin belt consists of a tightly packed hilly landscape, with many bogs and lakes found between the hills (Figure 3.2a, b). Soils within the catchment are mainly poorly drained gleys, with peat widely distributed throughout the northern section (Carson 2010). Land cover (based on CORINE data from 2006) is predominantly unimproved (62.5%) and improved (34.5%) pasture; however, small areas of forestry and peat bogs (3.0%) are also present in the upper section (EPA, 2016).

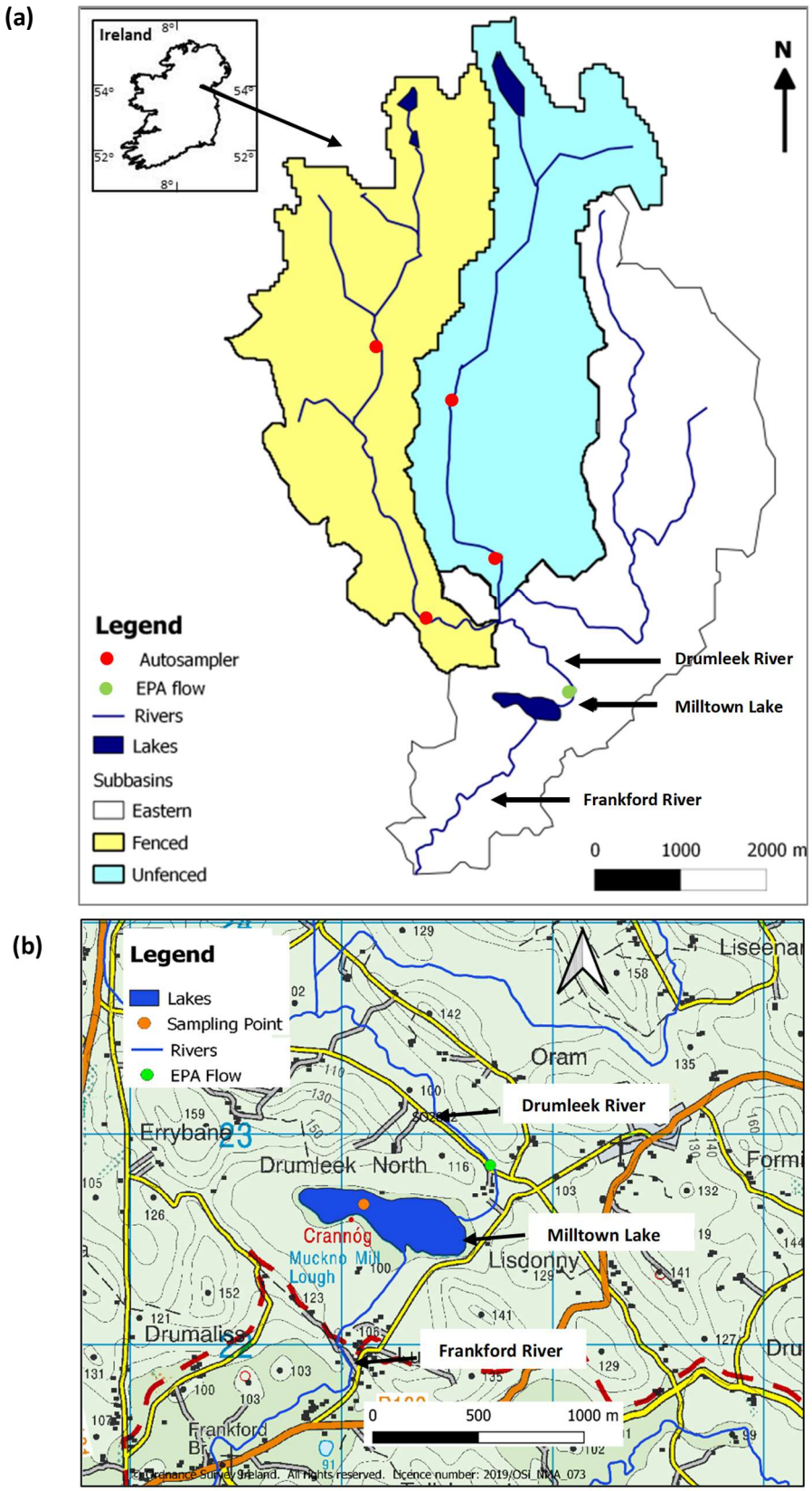

Figure 3.1 (a) Milltown Lake Catchment, Co. Monaghan, Ireland showing the western (fenced) and middle (unfenced) sub-catchments. Autosampler locations indicated by red dots, for the upper (north) and lower (south) sites on the fenced and unfenced tributaries. EPA staff gauge location indicated by green dot. Milltown Lake is shown at the bottom of the figure. **(b)** Milltown Lake, the orange dot indicates the sampling point (deepest point) within Milltown Lake, and EPA staff gauge location indicated by green dot.

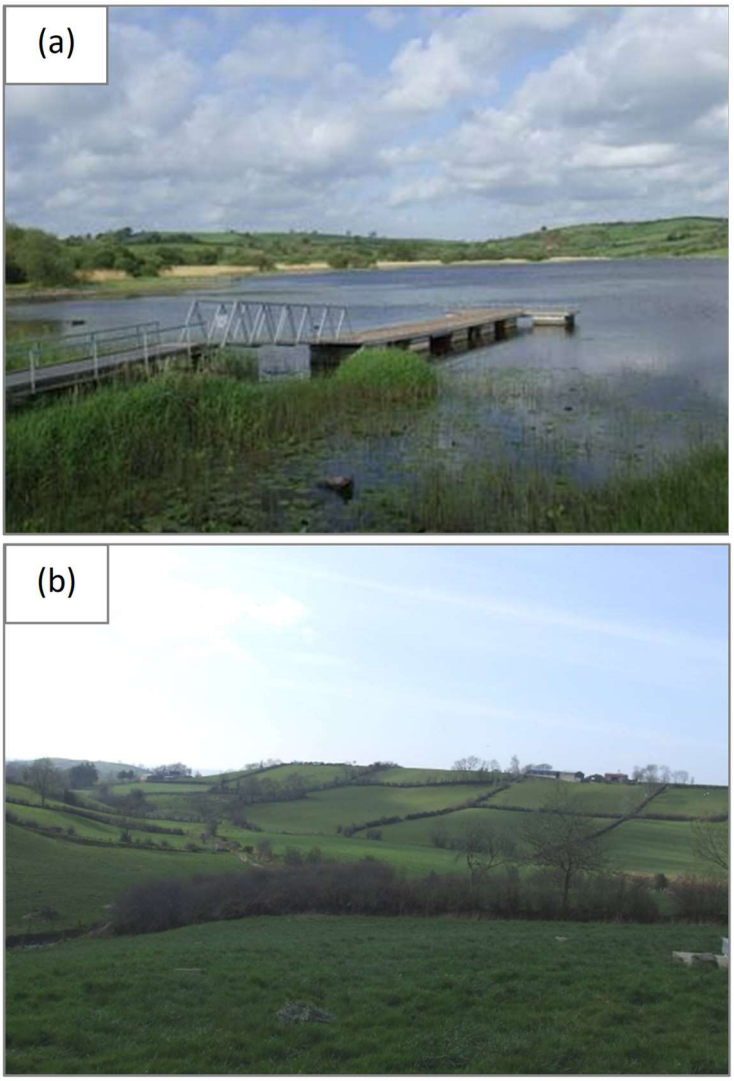

Figure 3.2 (a) Milltown Lake and **(b)** drumlin landscape of Milltown Lake Catchment.

The main land use within the catchment is grassland agriculture, including intensive beef and dairy farming. According to the 2010 Irish census, 60% of farming in the county is dedicated to beef rearing and 24% to dairy farming (Monaghan Co. Council, 2012). The farming enterprises in the Milltown Lake Catchment are comprised of 67% beef, 20% mixed (beef and sheep) and 7.8% dairy (Carson, 2010). A farm survey carried out in the Milltown Lake Catchment in 2008 reported that 74% of farmers were farming land that bordered a tributary on the Drumleek River system or Milltown Lake itself (Linnane et al., 2011). The survey also asked farmers in the catchment specific questions regarding fertiliser and slurry spreading practices. Of the farmers that responded, 88% reported leaving a buffer or margin when spreading near watercourses, although the size of the buffer varied widely from field to field.

The use of this study location builds on previous work carried out by the National Source Protection Pilot Project (NSPPP) (2005-2010), which focused on source protection for the water supply for the local GWS (Linnane et al., 2011). As part of the NSPPP, the western tributary had fencing installed at a distance of 1.5 m from the stream bank in 2008 with the aim of excluding livestock from having direct access to the river (Figure 3.3a, b). As is typical with such fencing, this also allowed the re-establishment of streamside vegetation, creating a vegetative strip. This width of 1.5 m was the minimum distance required for fencing under the 2009 Good Agricultural Practice for Protection of Waters Regulations guidelines (S.I. 101 of 2009) in Ireland and was also the maximum width that farmers in the catchment would agree to (Linnane et al., 2011). The other two tributaries remained unfenced. The middle tributary was chosen as an unfenced comparison to the fenced tributary (see Chapter 4), due to its similar characteristics, farming practices and land uses (Table 3.1; Figure 3.1). A survey of the fencing prior to the commencement of the current study in 2010 identified one unfenced cattle access point (CAP) in the upper headwaters of the western tributary. Eighteen CAPs were identified on the middle unfenced tributary.

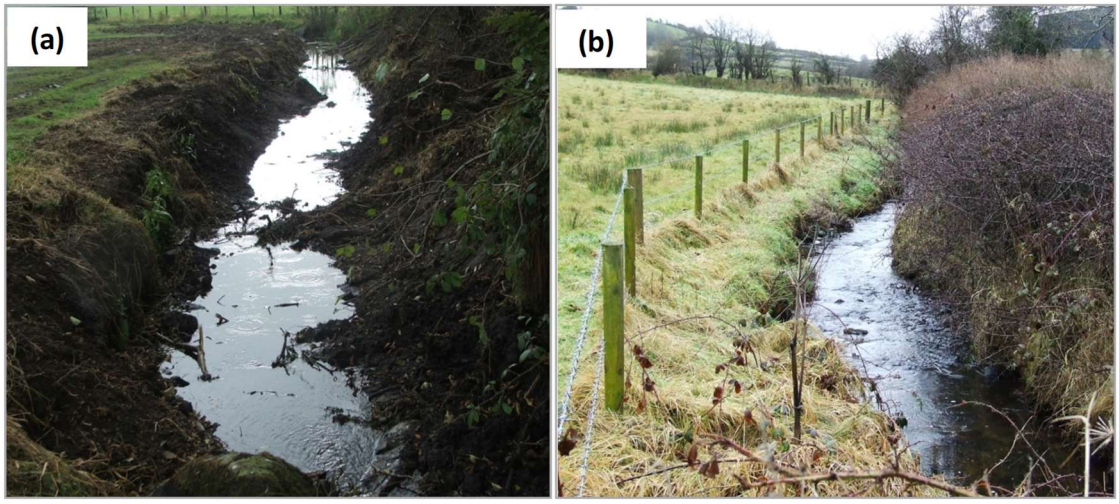

Figure 3.3 (a) Before fencing installed **(b)** after fencing (1.5 m from the stream bank) installed as part of the NSPPP in the Milltown Lake Catchment.

Table 3.1 Characteristics of the western (fenced) and middle (unfenced) stream reaches, in the Milltown Lake Catchment.

Characteristics	Catchment	Western tributary (fenced)	Middle tributary (unfenced)
Total area (km^2) excluding Milltown Lake	28.8	9.6	10.1
Tributary length (km)	24.6	8.4	6.3
Dwellings per tributary area (2010)	748	232	247
Cattle no. per tributary area (2010)	5554	1722	1833
*Upstream area above reach (km^2)		6.0	6.1
Upstream lake present		Yes	Yes
*Reach area (km^2)		3.6	4.0
*No. cattle access points in study reach		0	14
*Total length of cattle access points on reach (m)		0	48

* Reach refers to area between the upper and lower automated sampling sites on the tributaries as outlined in Figure 3.1a.

3.3 Stream discharge and meteorological data

In September 2005, an EPA staff gauge measuring stream discharge and water level on the Drumleek River (with an OTT Thalimede water level sensor) was installed in conjunction with the NSPPP and Monaghan County Council, approximately 500 m upstream (54°8'48"N; 6°42'15"W) from the inflow to Milltown Lake (Figure 3.1). Continuous stream discharge data (15 minute intervals) were available for this site from the Irish Environmental Protection Agency (EPA) Hydronet website (hydronet.epa.ie). The site was maintained by the EPA. Precipitation data for this study were obtained from the Coose weather station (10.4 km south-west for the Milltown Lake Catchment) and the Ballyhaise weather station (52 km south-west Milltown Lake Catchment) through Met Éireann (Table 3.2; Figure 3.4). Air temperature data were also available from Ballyhaise weather station. Additional data were obtained for the Clones Met Éireann station (42 km north-west) (Table 3.2; Figure 3.4). It should be noted that the Clones Met Éireann station closed in 2007.

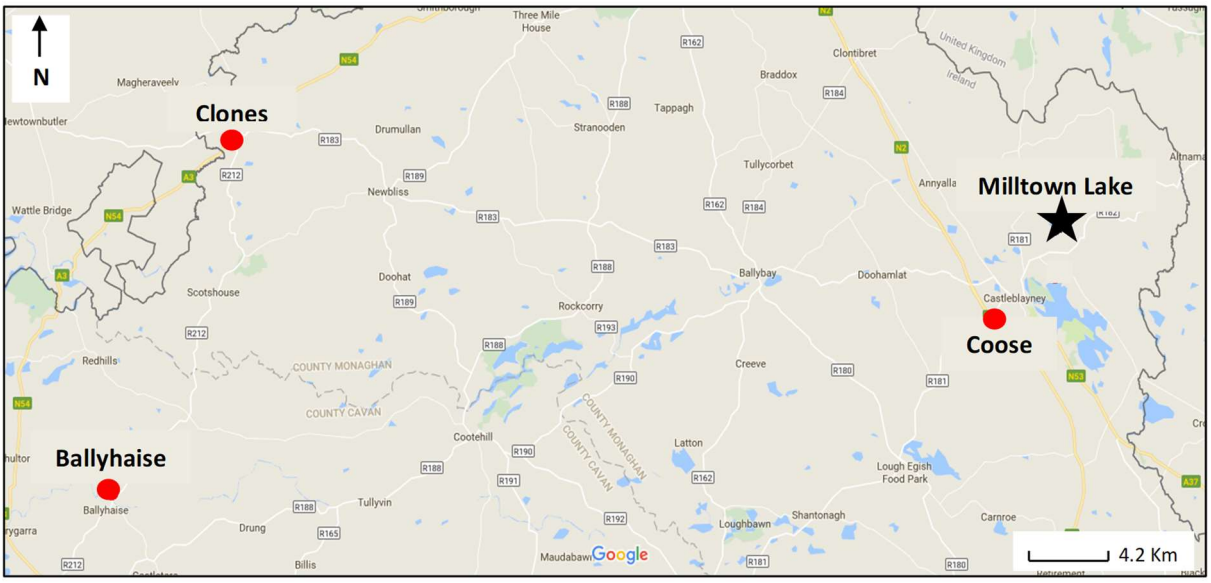

Figure 3.4 Location of the Ballyhaise, Clones and Coose Met Éireann weather stations in proximity to Milltown Lake.

Table 3.2 Long term average meteorological data at Met Éireann weather stations near Milltown Lake.

Long term averages	**Coose (2009 -2013)**	**Ballyhaise (2009 – 2013)**
Air temperature	not measured	9.0 ºC
Rainfall	1041 mm yr^{-1}	1001 mm yr^{-1}

3.4 Nutrient analysis

All nutrient analyses (TP, TN, NO_3-N, NO_2-N, NO_4-N and SRP) were carried out colormetrically using a flow injection auto-analyser (Lachat Quickchem®, Lachat 7 Instruments, Loveland, Colorado, USA). Samples analysed for dissolved nutrients were filtered (GF/C filters nominal pore size 1.2 µm) on the day of sample collection and stored in pre-acid washed and Milli-Q water rinsed 100 ml polyethylene bottles. Total P and TN were analysed in unfiltered samples using the persulfate method (4500-P-J) for simultaneous determination of TP and TN (APHA, 2005). The QuickChem® methods used to determine TP, TN, SRP, NH_4-N, NO_3-N and NO_2-N concentrations are outlined in Table 3.3. Total dissolved nitrogen (TDN) was calculated as the sum of NH_4-N, NO_3-N and NO_2-N.

Table 3.3 QuickChem® Methods used to determine phosphorus and nitrogen.

Parameter	QuickChem® Method	Detection Limit
TP	10-107-04-4-B	0.007 mg P L^{-1}
TN	10-115-01-4-B	0.046 mg N L^{-1}
SRP	10-107-06-2-L	0.007 mg P L^{-1}
NO_4-N	10-107-04-1-R	0.008 mg N L^{-1}
NO_3-N	10-115-01-1-V	0.016 mg N L^{-1}
NO_2-N	10-115-01-1-V	0.016 mg N L^{-1}

Calibration standards for all of the above methods were prepared from separate 1000 mg L^{-1} stock standard solutions from Inorganic™ Ventures. These were sodium nitrate ($NaNO_3$) for TN and NO_3-N, sodium nitrite ($NaNO_2$) for NO_2-N, ammonium chloride (NH_4Cl) for NH_4-N and ammonium phosphate ($(NH_4)_3PO_4$) for TP and SRP analysis. In-house quality control check standards were prepared from analytical grade chemicals that were made from the same compound used in the calibration standards but purchased from a different manufacturer, i.e. Acros Organics™. Quality control check standards and laboratory and field blanks were included at the start of an analytical run and periodically, thereafter, to assess for instrumental drift. In the case of TP and TN analysis, the calibration standard, quality control standard, field and laboratory blanks were digested with potassium persulphate in the same manner as the samples prior to analysis on the Lachat flow injection auto-analyser.

3.5 Automatic sensor deployment in Milltown Lake and calibration

Additional data for water quality parameters were collected from Milltown Lake (Chapter 5 and 6) using automatic sensors located on permanent monitoring platforms. The Milltown Lake monitoring platform (deployed in November 2011) was anchored at a fixed position at the deepest point of the lake (~ 10 m) (Figure 3.1b). The instrumentation installed on the platform included two dissolved oxygen (D-Opto) sensors, at depths of 1 m and 7 m, which recorded DO data (mg L^{-1} and % saturation) at 10 minute intervals. Data were downloaded from the DO sensors every 2 months. In addition, a chain of nine TidbiT temperature loggers (ONSET, Tidbit® v2 Temp Logger) were installed in Milltown Lake in April 2010 to allow for the

assessment of changes in physical structure. These sensors were mounted at 1 m depth intervals (1, 2, 3, 4, 5, 6, 7, 8 and 9 m) and recorded temperature data (ºC) at 10 minute intervals. Data from the temperature loggers were collected using a HOBO® Shuttle-U-DTW-1 on a quarterly basis. All sensors were cleaned monthly during the winter, bi-weekly during spring and autumn and on a weekly basis during the summer, using a non-abrasive cloth and distilled water.

3.6 Chlorophyll-*a* analysis

Chlorophyll-*a* samples (1 L) were filtered through GF/C filters, nominal pore size 1.2 µm. The filter papers were placed individually into 10 ml centrifuge tube and analysed on the day of sample collection. Extraction of Chl-*a* was carried out in the laboratory using a methanol (Emsure 96%) extraction method. Methanol (10 ml) was added to the centrifuge tube and heated at 75 ºC for five minutes. Samples were allowed to cool to room temperature and filter papers were removed from the tubes. The remaining methanol was then centrifuged at 3500 rpm for 8 minutes. The clear extract was transferred to a cuvette and analysed using a Shimadzu Spectrophotometer (UV-1800), set to measure absorbance at 665 nm and at 750 nm against a reference cell filled with methanol. The Chl-*a* concentrations (mg L^{-1}) were calculated according to the following equation (Standing Committee of Analysts, 1983).

$$\text{Chl-}a = 11.9 \times A \times V_e/V_s \times d \qquad \text{(Equation 3.1)}$$

Where A is the absorbance at 665 nm minus the absorbance at 750 nm of the extract; V_e is the volume of the extract (ml); V_s is the volume of the filtered sample (L); d is the path length of the optical cell (cm); and 11.9 is a coefficient. The factor 11.9 approximates to the reciprocal of the specific absorption coefficient at 665 nm for Chl-*a* in acetone (Standing Committee of Analysts, 1983). It includes an arbitrary assessment of absorbance contributed by other pigments (Standing Committee of Analysts, 1983).

3.7 Analysis of lake temperature profile data

Lake Analyzer is a visualisation tool for determining indices of mixing and stratification in lakes, providing standardised lake physical calculations including water density based upon temperature, thermal layers, thermocline depth, metalimnion depth, lake number, buoyancy frequency, Wedderburn number (Wn) and Schmidt stability (S) (Read et al., 2011) (http://lakeanalyzer.gleon.org/). Input data files required to run the programme include data on the lake hypsographic curve, water temperature profile, wind speed and a lake specific configuration file. The latter includes details of the lakes features such as maximum lake depth, height of wind speed instrument above the lake, and details of outliers for wind speed and temperature of the lake. The configuration file also outlines the data output resolution (daily/hourly) and an option on which figures to generate. For the current study lake temperature profile, S, buoyancy frequency, thermocline depth and Wn were used (Chapters 5 and 6).

3.8 Statistical methods

Detailed statistical analysis are outline in the subsequent chapters. Chapter 4 focuses on the nutrient export from a cattle based agricultural catchment and the effects of streamside fencing as a mitigation measure for the Milltown Lake Catchment. While Chapter 5 and Chapter 6 focuses on the local drivers of phytoplankton biomass during the spring/summer of 2012 and the spring of 2013 in Milltown Lake. Statistical analysis were carried out using the R statistical package version 3.2.2 (R Core Tea, 2015).

Chapter 4: The effects of streamside fencing on P and N concentrations in catchment streams of Milltown Lake

4.1 Abstract

Streamside fencing with vegetative buffer strips can be used as a mitigation measure to decrease nutrient and sediment loss from agricultural land to water and have been included in many European agri-environmental schemes. To date, limited research has been carried out within Europe on their effectiveness, particularly in western Europe which has a high-rainfall, oceanic climate. The work presented in this chapter investigated the effects of streamside fencing on stream water TP and TN concentrations in an intensive cattle-based agricultural landscape in north-east Ireland. The study was based on an upstream/downstream design and included a stream reach that had been fenced to exclude cattle five years before the study commenced (referred to as the fenced stream) and a separate unfenced stream reach on an adjacent tributary. The results indicated that exclusion fencing was effective in reducing TP and TN concentrations in the stream during the spring to autumn grazing period in 2011 (when slurry spreading was also permitted by Regulation). However, there was a significant increase in TP concentrations from upstream to downstream on this fenced reach during the following late winter/early spring, a period when slurry spreading was permitted by regulation, but cattle were still in winter housing. This behavioural difference was further evident in the differing concentration-discharge relationships for TP for both catchments in the Grazing season and TN during the Open slurry spreading period. The difference between the two study periods may reflect interaction with buffer strip vegetation, which would be greatest in the grazing season but lower in the second study period.

4.2 Introduction

Identifying the areas in the landscape that pose the greatest risk of nutrient losses to surface waters is a critical component of nutrient management (Sharpley et al., 1993; Shore et al., 2014). These small defined areas, which contribute much of the catchment's sediment, P and N, are

known as critical source areas (Jorgensen, 2009) and can include sites where livestock have direct access to watercourses (McDowell and Srinivasan, 2009). Streamside fencing is used as a method to exclude livestock from waterways (Galeone, 2000; Vidon et al., 2008; Miller et al., 2010). Fencing is often used in conjunction with other agricultural management practices such as riparian buffers, and off-stream watering for livestock. It is mainly used to target and reduce suspended sediment and nutrient inputs to surface waterbodies from un-vegetated or sparsely vegetated stream banks, caused by livestock tramping and excess grazing (Belsky et al., 1999; Centner et al., 1999; Galeone, 2006; Miller et al., 2010; Miller et al., 2011). The main effect of fencing is the reduction of nutrients from livestock directly defecating and urinating within watercourses (Thomas, 2002; Miller et al., 2010). However, fencing also allows for the establishment of vegetation in riparian buffer areas, which further aids in reducing the nutrient and sediment input to streams through filtering overland discharge and retention of nutrients in biomass (Galeone, 2006; Melland et al., 2014; Haddaway et al., 2016). Riparian buffer zones are permanently vegetated areas located between agricultural fields and the watercourse to which they drain (Heathwaite et al., 1996; Haddaway et al., 2016). Dorioz et al. (2006) analysed the mechanism of typical grassland buffer strips on the specific behaviour of P and concluded that buffers have the capacity to decrease particulate P transfer from surface water discharge paths, increasing residence time and allowing for further biochemical processes to develop. However, Stoate et al. (2009) showed that in temperate northern climates (The Netherlands, Finland, Sweden and the UK), grassy buffer strips were ineffective during spring when vegetation was underdeveloped, and rain was most severe. Reichenberger et al. (2007) also showed that, during storm discharge events, buffer strips tend to be less effective as they are more effective when dealing with slow, shallow moving overland discharge. Shallow moving discharge provides maximum contact time for the removal of pollutants by several physical processes, including deposition and infiltration (Centner et al., 1999).

To date, there have been limited studies focusing on the effect of exclusion fencing in areas with intensive, cattle-based agriculture in western Europe, where management practices and climate differ from those in the US, Canada and Australia (Conroy et al., 2016; Bragina et al., 2017). In Ireland, these differences include longer periods when cattle graze in fields (van den Pol van Daselaar et al., 2015; Chen and Holden, 2016), land application of slurry for most of the year and high rainfall from south-westerly air-masses from the Atlantic Ocean (Nolan et al., 2010). As part of the consultation process with specific environmental authorities for the new RBMP 2018-2021 running in Ireland, the requirement of specific measures needed to target nutrient pollution from agriculture were highlighted (Department of Housing, Planning, Community and Local Government, 2018). Measures put forward included raising awareness and implementing streambank fencing with bankside vegetation as a viable option for restricting cattle access to water courses and reducing nutrient pollution from diffuse agricultural sources.

The bulk of annual P transfers are associated with sudden and infrequent high discharge events (Jordan et al., 2005; Jordan et al., 2007). However, Jordan et al. (2005; 2007) also noted that some rivers, particularly in rural Ireland, may also be maintained in a eutrophic state between storm events by low-level nutrient inputs from point sources, e.g. OSWTS. In the current study, in addition to determining the viability of streamside fencing as a management option for nutrient level reduction, nutrient concentration responses during infrequent high discharge events were examined to gain insight into the processes that were operating in both a fenced and an unfenced stream reach. This included the overall nutrient-discharge relationships, and a small number of targeted sampling campaigns for individual events. Previous studies examining concentration-discharge relationships have provided valuable information on the likely P and N sources (Ide et al., 2008; Stutter et al., 2008; Bowes et al., 2009; Abell et al., 2013). This concept is based on examining the difference in nutrient concentrations on the rising

and falling limb of the storm hydrograph (Bowes et al., 2015) (Figure 4.1). If the concentration of nutrients increases on the rising limb and decreases on the falling limb, the hysteresis plot produces a clockwise loop in the concentration-discharge relationship (Bowes et al., 2015) (Figure 4.1). This is considered to be caused by a quick flushing of sediment or nutrients to the waterbody which may become exhausted by the end of the storm event and therefore, indicates a source close to the stream (Williams 1989; Bowes et al., 2015). An anti-clockwise loop is indicative of high particulate or dissolved nutrient concentrations in the falling limb of the storm hydrograph, signifying the sediment peak is lagging the discharge, providing evidence of longer transit times of water and sediment (Williams 1989; Bowes et al., 2015) (Figure 4.1). This suggests that the nutrient source may be further from the stream. Finally, a figure-of-eight configuration combines both the clockwise and anti-clockwise configuration, and is considered to be related to a shift in the form of the relationship between discharge and sediment or nutrients, and therefore the source, during the course of a single flood event (Williams 1989; Bowes et al., 2015). However, Lloyd et al., 2016 noted that many hysteresis loops may be difficult to classify easily into these groups, and care should be taken with interpretation as the same type of loop could occur for different reasons. Nevertheless, the study of concentration-discharge relationships during high discharge events using hysteresis can provide a valuable research tool to infer the likely contributing source areas and discharge pathways contributing to nutrient and sediment transport in catchments (Lloyd et al., 2016).

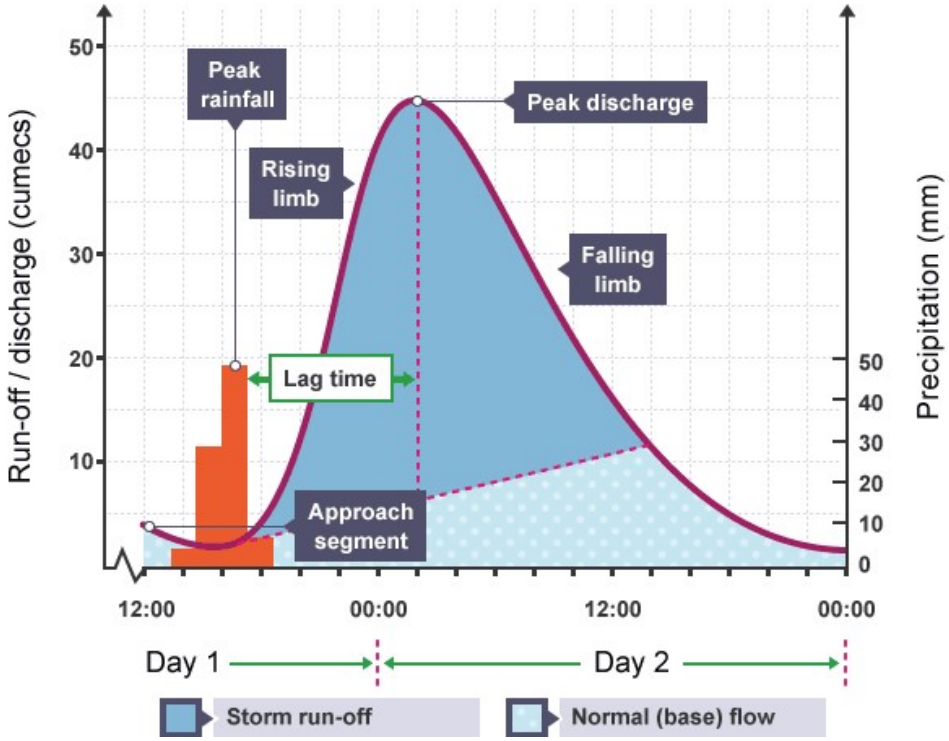

Figure 4.1 Storm hydrograph (www. geographyaslevelaqa.wordpress.com, 2016).

4.3 Aims

The primary aims of this chapter were to investigate the effects of agricultural management on P and N levels in catchment streams, including the effect of excluding cattle from stream waters, using fencing, as a mitigation measure. In addition, the chapter explored nutrient concentration/discharge relationships during different selected study time periods and selected discharge events to gain an insight into the processes operating in both the fenced and unfenced stream.

4.4 Methods and materials

Daily stream water sampling took place during three time periods between the 20th of April 2011 and the 16th of April 2012. Daily water samples were collected at four sampling points over three time periods that represented three main land management changes in the Irish agricultural calendar (Table 4.1). The main grazing period was further sub-divided into the Early Grazing (20th of April to 8th of June 2011) and Late Grazing period (9th of June to 31st of

October 2011), based on the expected time frame when grass for silage is normally cut in Ireland at the beginning of June. Best advice from Teagasc, the Irish agricultural authority, is that slurry spreading should take place immediately after silage is cut but before cattle are allowed to graze the grass (Teagasc, 2011) (Table 4.1). It is also important to note that in 2011, the period for slurry spreading was officially extended for two weeks beyond the GAP Regulations until the 31st of October due to abnormally high rainfall (Oireachtas, 2011).

Table 4.1 Field sampling categories and dates for this study between the 20th of April 2011 to the 16th of April 2012.

Study Period	Dates	n (days)	Agricultural Practices
Grazing	20th April to 31st October 2011	176	Cattle grazing the land and slurry spreading permitted under the GAP regulations
Early Grazing	20th April to 8th June 2011	50	
Late Grazing	9th June to 31st October 2011	126	
Closed	1st November to 17th November 2011	17	Slurry spreading prohibited under the GAP regulations and cattle still in housing
Open	4th February to 16th April 2012	63	Slurry spreading permitted under the GAP regulations and cattle still in housing

4.4.1 Site selection

An initial scoping study was carried out on all three tributary streams between the 11th of May and 2nd of September 2010. This study determined which of the two unfenced (middle and eastern) streams would be suitable for comparing with the previously fenced (western tributary) (Figure 3.1a). The study involved an initial water sampling programme and a catchment inspection. The fenced tributary was also walked to inspect for any CAPs. One potential CAP (~1.5 m), was identified, where a farmer had not hung up a gate, thus providing a potential CAP. Both stream reaches were also surveyed to ensure that there were no major inflows to the reach.

During the scoping study, weekly grab samples were collected on a Tuesday (17 sampling trips) at sites that had previously been used in the NSPPP (Linnane et al., 2011) along the western, middle and eastern tributaries (Figure 3.1a). The eastern tributary flowed directly through one farmyard area, a potential point source of nutrients, and was therefore, considered unsuitable for the current study. Based on the findings of the scoping study, an upper and lower site were selected on both the western fenced and the middle unfenced tributary (Figure 3.1a). The upper site on the fenced tributary was approximately 950 m downstream from a single CAP identified and a small area of forestry, elevated concentrations of TP were identified directly downstream from this location. Therefore, the study focused downstream from this location. These final two selected stream reaches had similar land practices, along with similar slope profiles, therefore, allowing for the best comparison of the effects of fencing on the western tributary (Table 3.1; Figure 4.2). Automated samplers were placed at the selected sites. The percentage of sub-catchment area draining into the stream was calculated for each stream reach (fenced: 3.6 km^2; unfenced: 4.0 km^2) (Table 3.1).

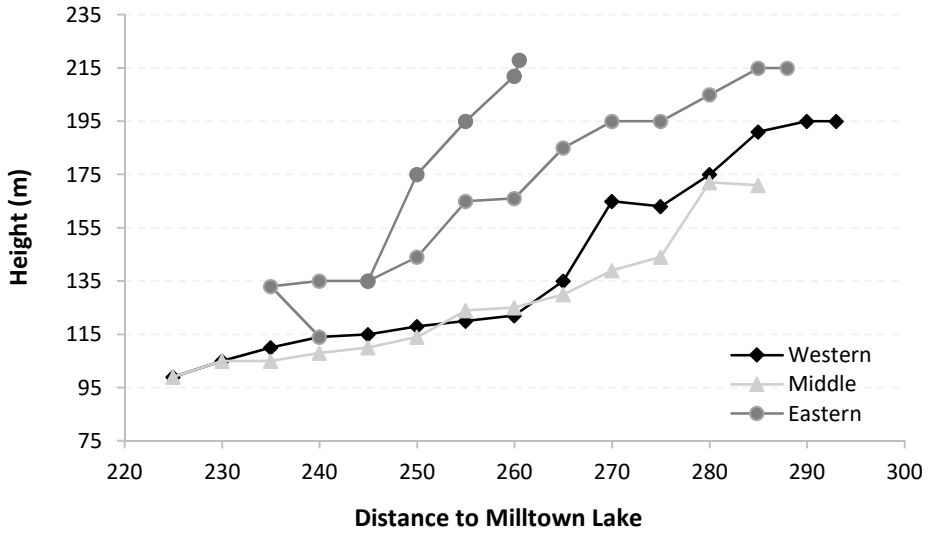

Figure 4.2 Distance from the source of the western, middle and eastern tributaries to Milltown Lake.

4.4.2 Sample collection and nutrient analysis

Automated samplers (ISCO® 6700, HACH® Sigma 900 Max and HACH® Sigma Streamline 800SL) were placed at the four selected sampling sites. Samplers were programmed to collect

six 50 ml samples per day (at 4 hour intervals), giving a final daily sample volume of 300 ml. The polyethylene sample bottles were pre-acid washed and rinsed with Milli-Q water. Sample bottles were collected weekly and stream discharge was measured at each of the four sites on that occasion (Global Water Flow Pro FP111). Continuous discharge data was obtained from the EPA staff gauge at the base of the Drumleek River (Section 3.3). Daily discharge rates at the four sampling sites were estimated from this data using the percentage catchment area draining into the stream at particular sampling points, the drainage area-ratio method (Archfield and Vogel, 2010). These estimated discharge rates showed a good correlation with the discharge rates measured at each site on the sampling dates ($r = 0.95$; $p < 0.0001$ (fenced upper site); $r = 0.93$; $p < 0.0001$ (fenced lower site) $r = 0.92$; $p < 0.0001$ (unfenced upper site) and $r = 0.87$; $p < 0.0001$ (unfenced lower site)). Conductivity ($\mu S\ cm^{-1}$), pH, DO in both ($mg\ L^{-1}$) and (% SAT) were measured using a YSI® 556 Handheld Multi-parameter Instrument or YSI Professional Plus Multi-parameter Instrument. The portable YSI probe was calibrated in the laboratory before carrying out field work and assessed periodically throughout the sampling day.

In addition, four high discharge events were sampled over a 24 hr period at the lower sites of the fenced and unfenced tributaries. These events included one during the main grazing season, in 2010 and 2011, and the first high-discharge event in autumn in each year. High discharge events were sampled, with the use of the above automated samplers, at the lower sites on the fenced and unfenced tributaries. Samplers were programmed to collect a 300 ml sample at hourly intervals, over the 24 hr sampling period. The sample bottles were treated in the same manner as stated above, prior to sample collection. Stream discharge, conductivity ($\mu S\ cm^{-1}$), pH, DO ($mg\ L^{-1}$ and % SAT), were measured at each of the two sites, before and after each event.

Nutrient analyses were carried out as described in Section 3.4. Total P and N concentrations were measured on all samples collected from the weekly sample collection and all samples collected for the high discharge events. Samples for dissolved nutrients were measured on the final two days of the weekly sampling programme and on all samples collected for the high discharge events, based on permitted holding times for analysis.

4.4.3 Data analysis

Statistical analysis were carried out using the R statistical package version 3.2.2 (R 195 Core Team, 2015). Significant differences in nutrient concentrations between the fenced and unfenced tributaries were determined using the non-parametric Mann Whitney U test (Helsel and Hirsch, 1992; Zuur et al., 2007) using the mgcv package (Wood, 2006) in R (version 3.2.5, R 195 Core Team, 2015). Generalized additive modelling (GAM) was used to determine the main climatic and hydrological drivers of change in TP and TN concentration for the lower sites in the fenced and unfenced streams, and for each of the management periods. The GAM analyses were carried out using the mgcv package in R (Wood, 2006). The residuals of the initial model and final model were checked for any breach of the assumption of heterogeneity using gam.check function in R. The final model was also checked for any breach of the assumption of independence by checking the autocorrelation function of the model residuals. The optimum or best fit GAM models were selected using the lowest Akaike Information Criterion (AIC) (Akaike, 1974; Zuur et al., 2009). The independent variables assessed included discharge (log transformed), air temperature, solar radiation (obtained from the Ballyhaise Met Éireann weather station) and rainfall (obtained from the Coose Met Éireann weather station).

Plots of relationships between concentration (TP, SRP, particulate P, TN and TDN) and stream discharge for each high discharge event were inspected to identify hysteresis that reflected consistent differences in the concentration between the rising and falling limbs of the

hydrograph (Bowes et al., 2015; Lloyd et al., 2016). The distinct features looked for were (1) clockwise, a quick flushing of sediment or nutrients to the waterbody which may become exhausted by the end of the storm event, therefore indicating a source close to the stream, (2) anti-clockwise, indicating high particulate or dissolved nutrient concentrations in the falling limb of the storm hydrograph, signifying that the sediment peak is lagging the discharge and (3) figure of eight behavior, considered to be related to a shift in the form of the relationship between discharge and sediment or nutrients, and therefore the source, during the course of a single flood event (Williams 1989; Bowes et al., 2015). Observed hysteresis was subsequently characterised for all four high discharge sampling events at the lower sites on the fenced and unfenced tributary.

4.5 Results

4.5.1 Meteorological and hydrology data

The weather during the sampling period was characterised by generally mild and wet conditions, typical for the region. The mean daily air temperature at the Ballyhaise weather station for the period between 20th of April 2011 to the 16th of April 2012 was 8.8 ºC. However, the maximum of 17.5 ºC was actually recorded on the 03rd of June 2011, with a minimum of -2.0 ºC on the 2nd of February 2012 (Figure 4.3a). Mean daily air temperature at the Ballyhaise weather station for the Grazing study period was relatively low at 11.0 ºC (mean of 9.5 ºC for the Early Grazing and 11.5 ºC for the Late Grazing period). During the Closed and Open periods, the mean daily air temperatures were 8.8 ºC and 6.9 ºC respectively (Table 4.2). Total annual and mean daily rainfall at the Coose weather station for the study period were 994 mm yr^{-1} and 2.7 mm day $^{-1}$ respectively, with a maximum rainfall of 32.7 mm day $^{-1}$ on the 11th of November 2011 (Figure 4.3b). Mean daily rainfall for the Grazing period was 2.9 mm day $^{-1}$ (2.0 mm day $^{-1}$ for the Early Grazing and 3.2 mm day $^{-1}$ for the Late Grazing period), while the values for the sampling days in the Closed and Open periods were 4.2 mm day $^{-1}$ and 1.2 mm day $^{-1}$, respectively (Table 4.2). Overall, there were 179 wet days (of 256 total sampling days)

recorded (days ≥ 1 mm of rain) during the overall study period. The wettest month was October 2011 (151 mm month^{-1}) while the driest month was March 2012 (19 mm month^{-1}) (Figure 4.3c).

Daily stream discharge at the EPA staff gauge on the Drumleek River ranged from a low of 0.04 m^3 sec^{-1} on the 4th of August 2011 to 8.81 m^3 sec^{-1} on the 25th of October 2011 (Figure 4.3b). Mean stream discharge for the Grazing period was 0.39 m^3 sec^{-1} day^{-1}, that for the Closed period sampled was 0.84 m^3 sec^{-1} day^{-1}, whilst the Open period had the lowest mean 0.24 m^3 sec^{-1} day^{-1} (Table 4.2). There was a weaker relationship between monthly rainfall and stream discharge between April to September 2011, when air temperature (and thus, evapotranspiration) was higher (r = 0.75) (Figure 4.3c). It is important to note that the Milltown Catchment is located on a poorly productive aquifer and has low permeability soil which include gleys and peat, the potential for loss to groundwater is low. In contrast, the correlation coefficient between rainfall and stream discharge during autumn and winter months was significantly higher at 0.92 (Figure 4.3c). No significant correlation was found between daily rainfall and stream discharge in the Grazing season, indicating that the precipitation which fell was evapotranspired.

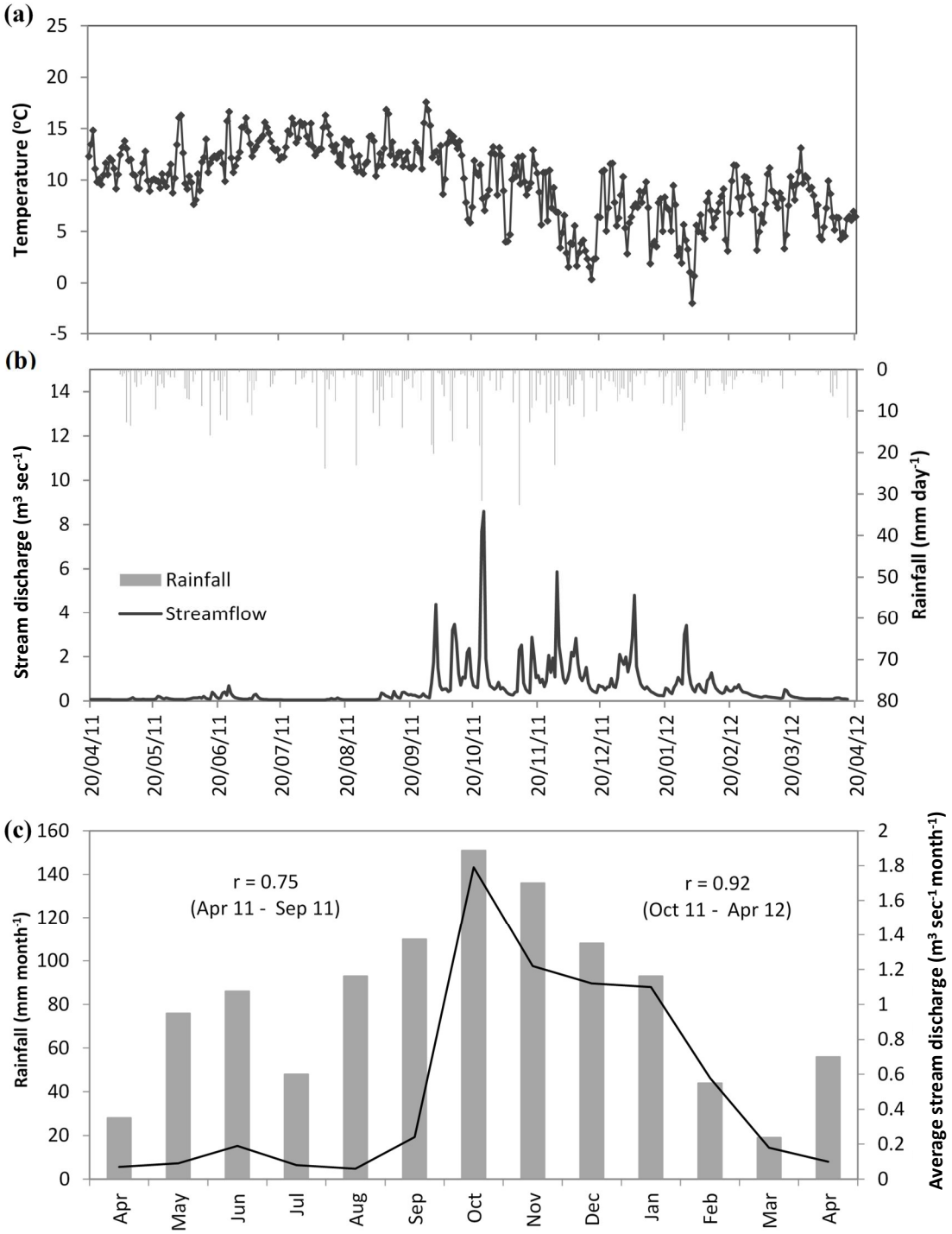

Figure 4.3 (a) daily mean air temperature (°C) at Ballyhaise Met Éireann weather station, **(b)** daily rainfall (mm day^{-1}) at Coose Met Éireann weather station and daily stream discharge (m^3 sec^{-1}) for the EPA staff gauge site on the Drumleek River, **(c)** Monthly rainfall (mm month^{-1}) (grey bars) and average monthly stream discharge data (m^3 sec^{-1} month^{-1}) (continuous black line) for the study period (April 2011 – April 2012). r = Pearson correlation for April to September 2011 and October 2011 to April 2012.

Table 4.2 Summary of meteorological data (Ballyhaise and Coose Met Éireann weather station) and hydrological data (EPA staff gauge on the Drumleek River) for the main study periods. n denotes the number of days in each period.

Period	Mean daily air temperature (Ballyhaise) (^oC)	Mean daily rainfall (Coose) (mm day^{-1})	Cumulative rainfall (Coose) (mm)	Max daily rainfall (Coose) (mm day^{-1})	Mean daily stream discharge (m^3 sec^{-1})	n
Overall	8.8	2.7	994	32.7	0.57	362
Grazing	11.0	2.9	563	31.6	0.39	176
Early Grazing	9.5	2.0	98	13.5	0.08	50
Late Grazing	11.5	3.2	465	31.6	0.49	126
Closed	8.8	4.2	71	32.7	0.84	17
Open	6.9	1.2	78	11.6	0.24	63

4.5.2 General nutrient concentrations at the lower sites of the fenced and unfenced tributary

Total P concentrations measured at the lower sites on both the fenced and unfenced stream reaches were high (Figure 4.4). Peaks in concentration were observed throughout the sampling periods and were generally related to high discharge events. During the Grazing season, the fenced tributary had the highest peaks in concentration, in general, with the exception of one very high TP concentration (1.43 mg TP L^{-1}) on the 12th of June 2011 for the lower site on the unfenced reach (Figure 4.4c). It is important to note that this spike in concentration was apparent for all nutrient parameters measured on that day and may be attributed to the runoff from land due to recent rainfall, from slurry spreading on freshly cut silage fields. The fenced tributary also had the higher TP concentrations throughout the Closed period (Figure 4.4e). Total P concentrations in the Open period were marginally higher for the unfenced tributary, with three well defined high concentration peaks seen towards the early stages. However, toward the end of the Open period there was a shift, with TP concentrations higher in the fenced tributary (Figure 4.4g).

Peaks in TN concentration were observed throughout the period, once again commonly related to high discharge events (Figure 4.4). During the Grazing season, for example, the highest peaks for the two lower sites on the stream reaches occurred at the downstream site on the unfenced

tributary, with two very high concentrations (6.57 mg TN L^{-1} and 4.97 mg TN L^{-1}) on the 12th of June 2011 and 19th of June 2011 (Figure 4.4d). Total N concentrations were higher in the unfenced tributary throughout the Closed period (Figure 4.4f). During the Open period, TN concentrations were generally higher in the unfenced tributary, peaking on the 18th of March 2011 (Figure 4.4h). However, a peak in TN concentration was seen in the fenced reach (2.00 mg TN L^{-1}) on the 19th of February 2011, which was not reflected in the unfenced stream reach (Figure 4.4h). This peak in TN concentration coincided with a concentration peak in TP for both stream reaches (Figure 4.4g).

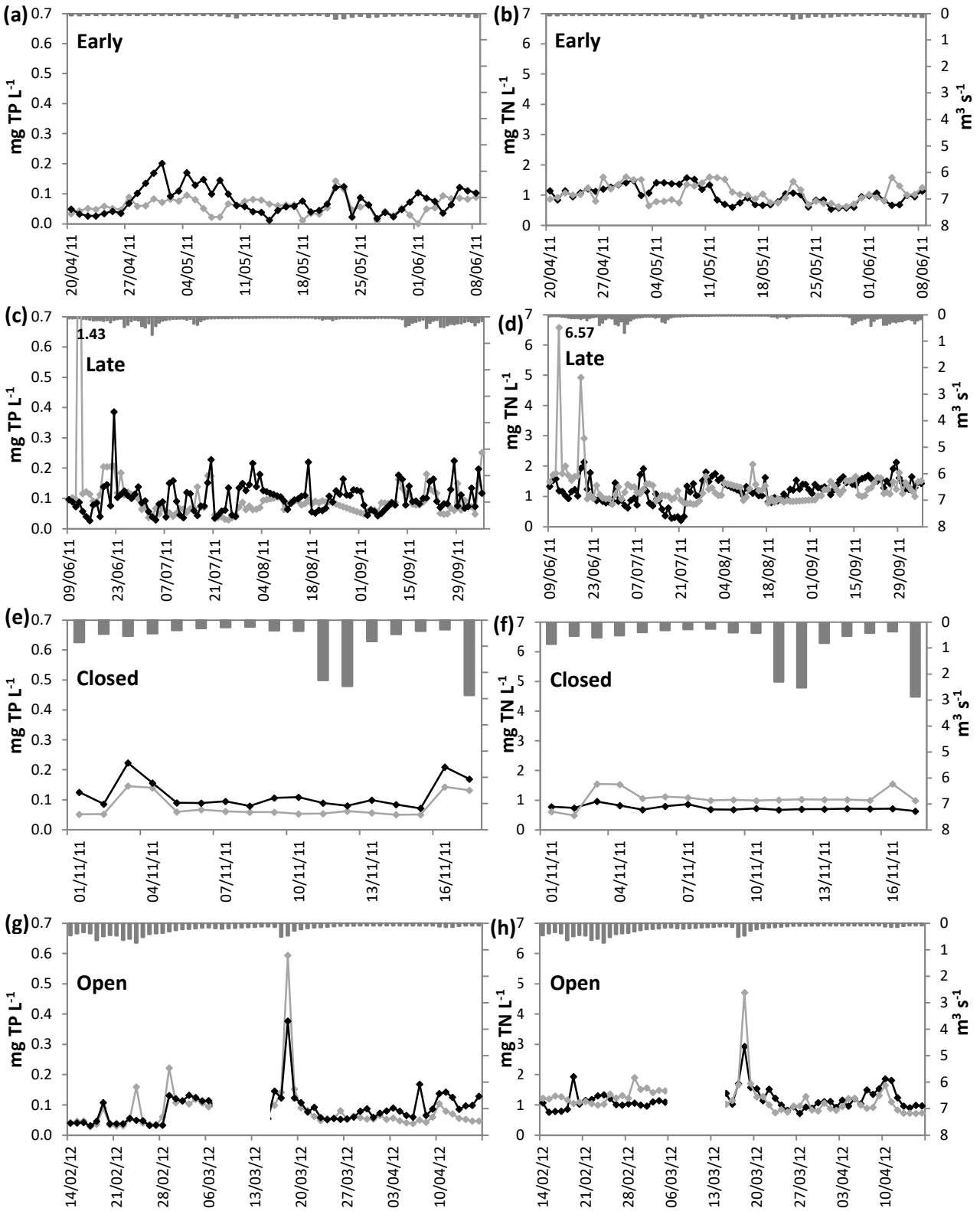

Figure 4.4 Daily TP concentration (mg TP L^{-1}) during the (**a**) Early Grazing, (**c**) Late Grazing, (**e**) Closed and (**g**) Open periods and daily TN concentration (mg TN L^{-1}) during the (**b**) Early Grazing, (**d**) Late Grazing, (**f**) Closed and (**h**) Open periods, for the lower sites on the fenced (black) and unfenced (grey) tributaries. Stream discharge from the EPA gauge is shown as grey bar. Note difference in scales between TP and TN figures.

4.5.3 Upstream to downstream nutrient concentration change

The changes in TP and TN concentration from upstream to downstream varied for both management period and type of nutrient. It was of note, also, that the median TP concentrations for the total study period were higher for the fenced stream reach at the upstream and downstream sites (both were 0.091 mg TP L^{-1}) than for the unfenced stream at the upstream (0.057 mg TP L^{-1}) and downstream (0.060 mg TP L^{-1}) sites. In contrast, both sites on the unfenced tributary had greater TP concentration ranges, in particular for the upper limit: (upstream: 0.012 – 0.127 mg TP L^{-1} and downstream: 0.010 – 0.106 mg TP L^{-1}). The equivalent ranges for the fenced tributary sites were 0.011 – 0.128 mg TP L^{-1} (upstream) and 0.012 - 0.125 mg TP L^{-1} (downstream). For the dates on which SRP data were available (weekly intervals), SRP accounted for, on average, 46% of the TP fraction for both the upper and lower sites on the fenced tributary and 46% for the upper and 44% for the lower sites on the unfenced tributary, indicating that c. 55% of TP was in particulate form at all four sites.

In the Early Grazing period, the two stream reaches differed in the pattern of change in TP concentrations as water travelled between the upper and lower autosampler sites. Despite the higher overall TP concentrations for the fenced reach, there was a significant decrease in TP concentration on this reach (median for upper site: 0.110 mg TP L^{-1}; median for lower site 0.065 mg TP L^{-1}; $p = <0.001$) between the upstream and downstream sites (a distance of 3.1 km), indicating a net retention of TP over this stream reach. Conversely, there was a significant increase between the upstream (0.034 mg TP L^{-1}) and downstream (0.060 mg TP L^{-1}) sites on the unfenced reach (a distance of 2.3 km) ($p = <0.001$), indicating net release of TP along this reach (Table 4.3; Figure 4.5a, e). This pattern, of a significant decrease in concentration as water travelled down the reach, was also apparent for the fenced site in the Late Grazing period, with median concentrations of 0.104 mg TP L^{-1} at the upstream site and 0.091 mg TP L^{-1} at the downstream site ($p = <0.001$). In contrast, the median TP concentration was again significantly

higher at the lower unfenced site than at the upstream site for that reach (0.057 mg TP L^{-1} upstream; 0.082 mg TP L^{-1} downstream to) ($p = <0.001$) indicating increased input of TP as the water travelled along the reach (Table 4.3; Figure 4.5b, f). During the subsequent short (2.5 weeks) sampling period in the Closed period, when slurry spreading was prohibited and cattle were also housed, there was no significant difference between TP concentrations at the upstream and downstream sites for either of the two stream reaches (Table 4.3; Figure 4.5c, g).

The patterns in upstream-downstream median TP concentration between the two streams did not persist through to the Open spreading period. During this sampling period (slurry spreading was again permitted, and cattle were still housed), the median TP concentration on the fenced tributary was lower for the upstream site (0.057 mg TP L^{-1}) compared to the equivalent site on the unfenced tributary (0.110 mg TP L^{-1}). However, the median concentration at the downstream site on the fenced tributary was now statistically higher that that at the upstream site, that is the concentration increased as water travelled down the reach (median for upper site: 0.057 mg TP L^{-1}; median for lower site 0.079 mg TP L^{-1}; $p = <0.05$), while the upstream site on the unfenced tributary was statistically lower (median for upper site: 0.110 mg TP L^{-1}; median for lower site 0.060 mg TP L^{-1}; <0.001) (Table 4.3; Figure 4.5d, h).

Table 4.3 Median TP and TN concentrations for the fenced and unfenced, upstream (US) and downstream (DS) sites (mg L^{-1}) during the Total, Early and Late Grazing, Closed and Open time periods, together with 25th and 75th percentiles. Significance levels for the Mann Whitney U test are also presented.

	Period		n	Median (mg L^{-1})	Q (25th)	Q (75th)	W	P
TP Fenced	Total study	US	256	0.091	0.011	0.128	9534	<0.001
		DS	256	0.091	0.012	0.125		
	Early Grazing	US	50	0.110	0.076	0.140	1725	<0.001
		DS	50	0.065	0.040	0.104		
	Late Grazing (& extension period)	US	126	0.104	0.086	0.124	9489	<0.001
		DS	126	0.091	0.070	0.124		
	Closed	US	17	0.103	0.083	0.128	140	ns
		DS	17	0.095	0.086	0.125		
	Open	US	63	0.057	0.048	0.081	1531	<0.05
		DS	63	0.079	0.055	0.111		
TP Unfenced	Total study	US	256	0.057	0.012	0.127	11062	<0.001
		DS	256	0.060	0.010	0.106		
	Early Grazing	US	50	0.034	0.027	0.053	786	<0.001
		DS	50	0.060	0.046	0.081		
	Late Grazing (& extension period)	US	126	0.057	0.041	0.101	5553	<0.001
		DS	126	0.082	0.062	0.106		
	Closed	US	17	0.055	0.049	0.061	116	ns
		DS	17	0.059	0.053	0.067		
	Open	US	63	0.110	0.061	0.127	2738	<0.001
		DS	63	0.060	0.047	0.099		
TN Fenced	Total study	US	256	1.000	1.000	1.630	10911	<0.001
		DS	256	1.030	1.030	1.483		
	Early Grazing	US	50	1.160	0.950	1.265	1507	ns
		DS	50	0.994	0.762	1.202		
	Late Grazing (& extension period)	US	126	1.425	1.183	1.630	10146	<0.001
		DS	126	1.225	0.919	1.483		
	Closed	US	17	0.691	0.644	0.711	84	<0.05
		DS	17	0.718	0.693	0.782		
	Open	US	63	0.943	0.822	1.163	1278	<0.001
		DS	63	1.114	0.988	1.282		
TN Unfenced	Total study	US	256	0.093	0.930	1.979	12085	<0.001
		DS	256	1.090	1.090	1.390		
	Early Grazing	US	50	0.699	0.597	1.004	583	<0.001
		DS	50	1.020	0.809	1.310		
	Late Grazing (& extension period)	US	126	0.911	0.701	1.298	559	<0.001
		DS	126	1.120	0.913	1.390		
	Closed	US	17	0.968	0.923	1.000	64	<0.05
		DS	17	1.020	0.994	1.090		
	Open	US	63	0.902	0.789	1.979	944	<0.001
		DS	63	1.160	0.956	1.310		

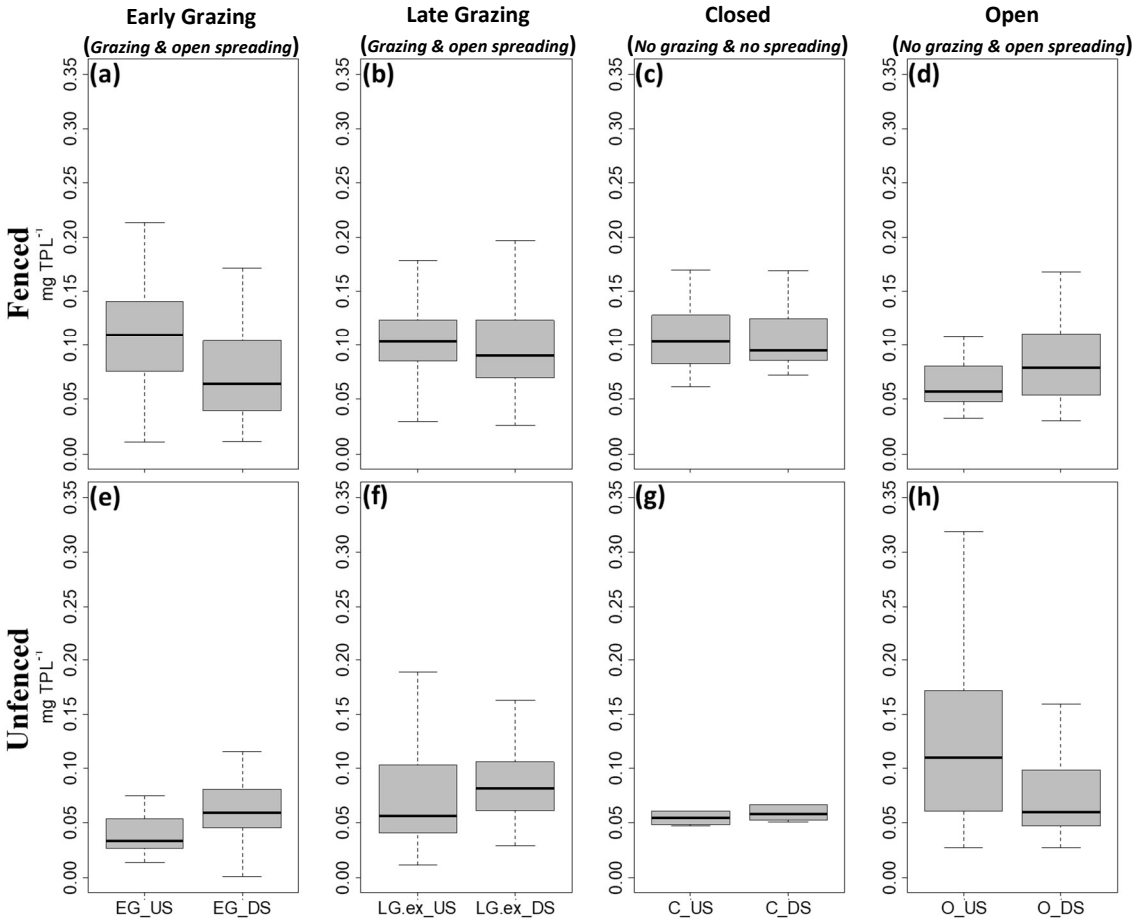

Figure 4.5 Median TP concentrations for the fenced (**a**, **b**, **c** and **d**) and unfenced (**e**, **f**, **g** and **h**) upstream (US) and downstream (DS) sites (mg TP L^{-1}) for the Early Grazing (EG, n = 50), Late Grazing including extension period (LG.ex, n = 126), Closed (C, n = 17), and Open (O, n = 63) periods. The whiskers indicate the maximum and minimum concentrations.

Median TN concentration for the total study period for the upper site on the fenced tributary (1.00 mg TN L^{-1}) was slightly higher (by 1.08 times) than the equivalent site on the unfenced tributary (0.93 mg TN L^{-1}). However, this relative difference was lower than that for TP. At the lower sites, the fenced tributary had a slightly lower median TN concentration (1.03 mg TN L^{-1}) compared to the unfenced tributary (1.09 mg TN L^{-1}). This difference was also apparent in the ranges for the upper and lower sites of the two tributaries (fenced: upper site 1.00 mg TN L^{-1} and fenced lower site 1.03 mg TN L^{-1}) which were again greater for the unfenced tributary (unfenced: upper site 0.93 mg TN L^{-1} and lower site 1.09 mg TN L^{-1}). On the sampling dates on which TDN data were available, TDN accounted for on average a higher percentage of the total load than was observed for TP: 74% of the TN fraction for the upper and lower sites on the fenced tributary, and 75% for the upper and 77% for the lower sites on the unfenced tributary.

For the Early Grazing period, the relative difference in TP concentration that was observed between the upstream and downstream sites on the fenced reach was not apparent for TN, that is, there was no significant difference between the concentration for upstream site (1.160 mg TN L^{-1}) and that for the downstream site (0.994 mg TN L^{-1}) (Table 4.3). In contrast, the lower site on the unfenced tributary (1.020 mg TN L^{-1}) had a significantly higher median TN concentration than the upstream site (0.699 mg TN L^{-1}) ($p = <0.001$) (Table 4.3; Figure 4.6a, e).

In the Late Grazing period, there was a slight but significant decrease in concentration between the upper (1.425 mg TN L^{-1}) and lower sites (1.225 mg TN L^{-1}) on the fenced reach ($p = <0.001$). In contrast, there was a slight but significant increase in concentration for the two sites on the unfenced reach (from 0.911 mg TN L^{-1} to 1.120 mg TN L^{-1} ($p = <0.001$) (Table 4.3; Figure 4.6b, f). During the Closed spreading period, when livestock were also housed, the unfenced reach had a median TN concentrations of 0.968 mg TN L^{-1} upstream and 1.120 mg TN L^{-1} downstream while those for the fenced reach were 0.691 mg TN $L^{-1}$and 0.718 mg TN L^{-1} upstream and downstream respectively (Table 4.3). This slight increase in concentration was significant for both the fenced and unfenced reach (Table 4.3; Figure 4.6c, g).

During the Open period and again in contrast to TP, there was net increase in TN concentrations from the upper to the lower sites ($p = <0.001$) (Table 4.3; Figure 4.6d, f). The median TN concentration for the upper site on the fenced tributary was 0.943 mg TN L^{-1} compared to 1.114 mg TN L^{-1} at the lower site (Table 4.3). The unfenced stream reach also indicated a significant increase in concentration and therefore, net release during the Open period (upper site 0.902 mg TN L^{-1}; lower site 1.160 mg TN L^{-1}).

In summary, the pattern of change in total nutrient concentrations included a significant downstream decrease in both TP and TN concentration for the fenced reach during the Grazing season, with, in contrast, significant increases in both TP and TN concentrations for the unfenced reach during the same period. These patterns reversed for TP only during the Open period, with a significant downstream increase in TP concentration for the fenced reach and a significant decrease in TP concentration for the unfenced reach. Both reaches had a significant downstream increase in TN concentration during the Open period.

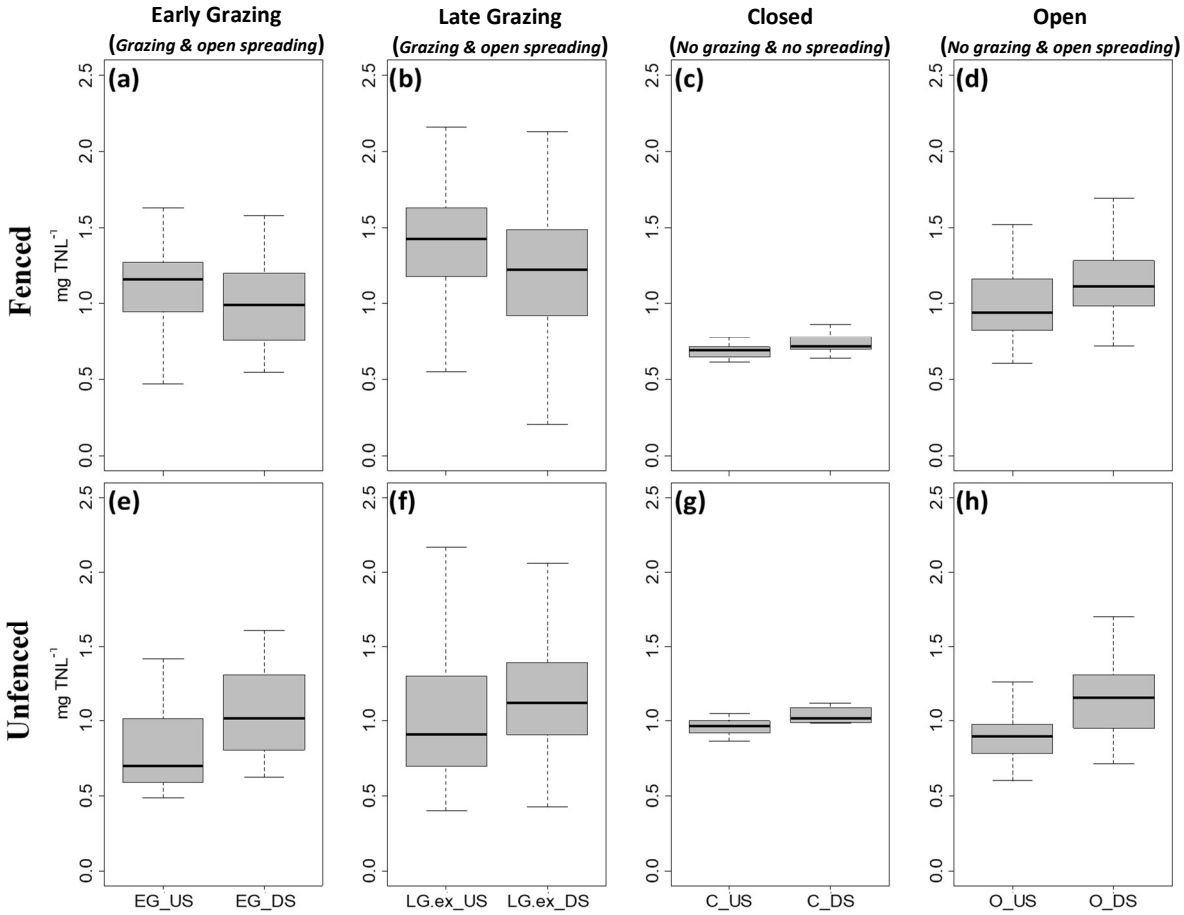

Figure 4.6 Median TN concentrations for the fenced (**a**, **b**, **c** and **d**) and unfenced (**e**, **f**, **g** and **h**) upstream (US) and downstream (DS) sites (mg TN L^{-1}) for the Early Grazing (EG, n = 50), Late Grazing including extension period (LG.ex, n = 126), Closed (C, n = 17), and Open (O, n = 63) periods. The whiskers indicate the maximum and minimum concentrations.

Overall, the annual TP and TN loads estimated based on the daily concentration data from this study were lower for the fenced (0.57 kg TP ha^{-1} yr^{-1} and 5.99 kg TN ha^{-1} yr^{-1}) tributary compared to that of the unfenced tributary (0.77 kg TP ha^{-1} yr^{-1} and 7.24 kg TN ha^{-1} yr^{-1}). The

estimated annual loads exported from the fenced catchment represented 74% and 83% of the loads from the unfenced catchment for TP and TN respectively.

4.5.4 Drivers of nutrient concentrations in the fenced and unfenced tributary

The optimum GAM for the TP concentration data at the lower site on the fenced tributary during the overall Grazing period (20th of April to 30th of October 2011) had one significant smoother (log transformed stream discharge – L.Flow) but this explained only 12% of deviance (Table 4.4; Figure 4.7a). The smoother describing the relationship between TP concentration and L.Flow for the fenced tributary indicated higher values at both low and high discharges (Figure 4.7a). Other weather related variables e.g. air temperature and rainfall were not significant. In contrast, the optimum GAM for TP concentration in the unfenced reach during the same period included two smoothers (L.Flow and air temperature) and explained 23% of variance (Table 4.4; Figure 4.7b; Figure 4.8). Here, the smoother describing the relationship between TP concentration and L.Flow had a very different pattern to that for the fenced reach, with low TP concentrations at low stream discharge, and a generally linear increase at higher discharges (Figure 4.7b).

The only significant term in the optimum model for the unfenced reaches in either time period was L.Flow. In contrast to TP, the smoothers between TN concentration and L.Flow for the Grazing period indicated similar relationships for both the fenced and unfenced reaches (Figure 4.7c, d), which were also relatively similar in pattern to that for TP concentration for the fenced reach. The smoothers describing the relationship indicated high TN concentration associated with both low stream discharges and at higher discharges, with a decrease at low to moderate discharges. The deviance explained by L.Flow was 19% for the fenced tributary and 13% for the unfenced tributary (Table 4.4; Figure 4.7c, d). The relationships between TP and L.Flow were not significant for either site during the Open period (14th of February to 16th of April

2012). However, the optimum GAMs for TN again indicated differing concentration-discharge behaviours between the fenced and unfenced tributaries. The smoother describing the relationship between TN concentration and L.Flow for the fenced tributary explained 27% of the deviance (Table 4.4). There was no clear direction for this relationship during lower and medium discharge periods, however, as discharge increased above 0.3 m^3 sec^{-1}, TN concentration then decreased (Figure 4.7e). In contrast, and similar to TP in the Grazing season, TN concentrations gradually increased with stream discharge for the unfenced tributary during the Open period (Figure 4.7f). The optimum GAM explained 18% of the deviance (Table 4.4).

Table 4.4 Generalized additive models for the lower sites on the fenced and unfenced tributary for TP and TN concentrations (mg L^{-1}), during the grazing period including extension period and TN concentration (mg L^{-1}) for the Open period.

Period		Site	parameter	N	edf	P	R^2 adj	% dev
Grazing	TP	Fenced	L.Flow	176	4.11	0.0024	0.10	12.0
		Unfenced	L.Flow	176	5.73	0.0235	0.19	22.8
			Air_Temp	176	3.10	0.0164		
	TN	Fenced	L.Flow	176	4.81	2.41e-05	0.16	18.6
		Unfenced	L.Flow	176	4.30	0.0012	0.10	12.6
Open	TN	Fenced	L.Flow	63	7.19	0.0566	0.17	26.7
		Unfenced	L.Flow	63	1.92	0.0095	0.15	17.9

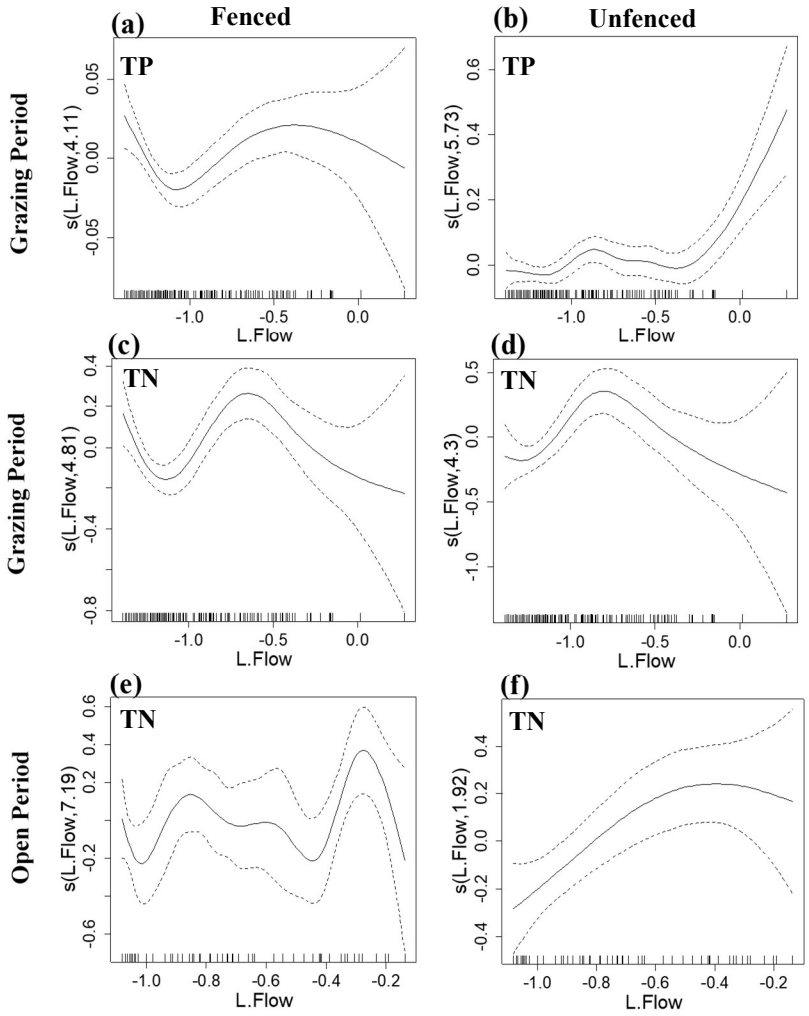

Figure 4.7 Estimated smoothing curves in the Grazing periods including extension period for TP concentrations (**a**) L.Flow fenced, (**b**) L.Flow unfenced and TN concentrations (**c**) L.Flow fenced, (**d**) L.Flow unfenced, lower reaches. Estimated smoothing curves in the Open period for TN concentrations (**e**) L.Flow fenced and (**f**) L.Flow unfenced, lower reaches. The solid line is the smoother and dotted lines indicate the 95% confidence intervals.

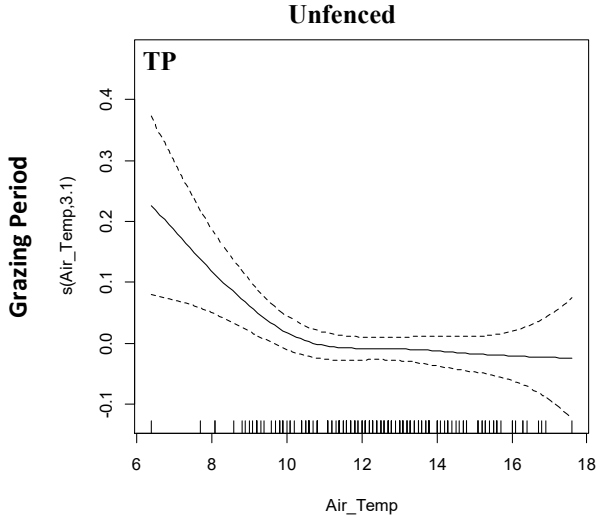

Figure 4.8 Estimated smoothing curves in the Grazing period including extension period for TP concentrations, for Air_Temp unfenced lower reach. The solid line is the smoother and dotted lines indicate the 95% confidence intervals.

4.5.5 Concentration-discharge relationships at a sub-daily scale

During the Grazing season of 2010 and 2011, nutrient concentrations over the time period of four high discharge events (11th- 12th of July 2010, 7th - 8th of September 2010, 25th - 26th of June 2011 and 2nd - 3rd of October 2011) were sampled at the lower sites on the fenced and unfenced tributary (Table 4.5; Figure 4.9). These included the first large high discharge event in autumn after a drier period in each of the two years, and one mid-summer but lower magnitude discharge event. A summary of the weather and stream discharge data for the high discharge events sampled in 2010 and 2011 is given in Table 4.5.

Table 4.5 Summary of meteorological data (Coose Met Éireann weather station) and hydrological data (EPA staff gauge) for the four high discharge events sampled during the grazing season in 2010 and 2011.

Date	Cumulative rainfall (7 day previous) (mm)	Cumulative rainfall (during event) (mm)	Max stream discharge (during event) (m^3 sec^{-1})	Mean stream discharge (during event) (m^3 sec^{-1})
11th – 12th July 2010	10.8	8.4	1.4	0.3
7th – 8th Sep 2010	18.1	90.8	11.9	6.2
25th – 26th June 2011	15.6	18.9	0.5	0.2
2nd – 3rd Oct 2011	7.4	36.4	4.6	2.8

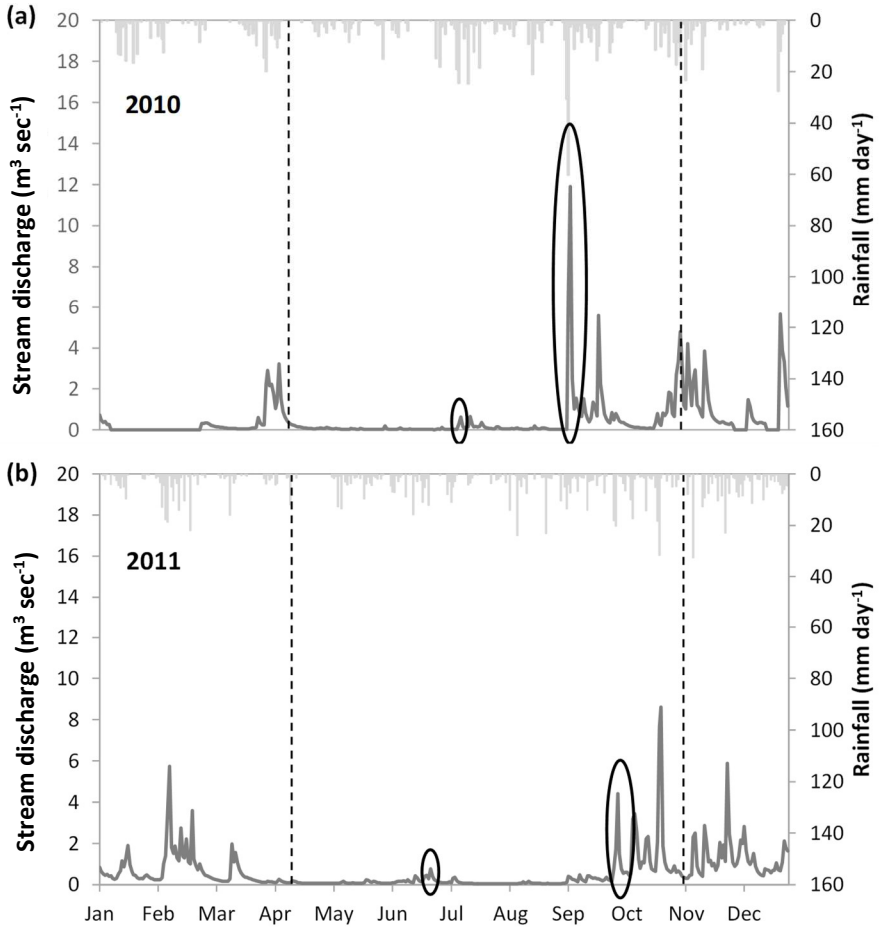

Figure 4.9 Stream discharge (m^3 sec^{-1}) from the EPA gauge is shown as grey line and daily rainfall (mm) from Coose Met Éireann weather station for (**a**) 2010 and (**b**) 2011. The events circled indicate the high discharge event sampled. The area between the dashed black lines indicates the Grazing period.

No consistent differences between the fenced and unfenced tributaries in the concentration-discharge patterns emerged across the hysteresis graphs for the four events sampled. However, there were some clear differences in behaviour, especially for the July and September 2010 events (Figure 4.10; Figure 4.11). During the initial mid-summer lower discharge event in July 2010 (maximum discharge = 1.4 m^3 sec^{-1}), TP concentrations were generally higher for the fenced tributary site (mean TP concentration: fenced 0.18 mg L^{-1}; unfenced 0.14 mg L^{-1}) (Table 4.6; Figure 4.10). Total P concentration in both tributaries increased rapidly on the rising limb of the event, indicating an initial washout of TP as discharge increased. While concentrations then fell on the falling limb for the unfenced site (clockwise hysteresis), the fenced tributary had a second increase in TP concentrations midway through the event on the falling limb, as indicated by a figure-of-eight pattern (Table 4.6; Figure 4.10). For both tributaries, the particulate P concentration displayed a clockwise pattern, indicating high particulate P wash-

out with rising stream discharge and then a drop in concentration as stream discharge decreased (Table 4.6; Figure 4.10). The concentration range for both sites was similar for SRP, but the pattern again differed, with a figure-of-eight pattern being observed for the fenced site, suggesting a second pulse in SRP being delivered to the stream, while there was a clockwise pattern for the unfenced site with falling concentrations as discharge fell (Figure 4.10).

The September event in 2010 was one of the highest discharge events recorded for the Drumleek River discharge gauge site, reaching 12.8 m^3 sec^{-1} at its peak (Figure 4.9a). It came after a relatively dry period in August and early September. Both tributaries had an initial flush of TP from the catchment as the stream discharge increased, with concentration increasing from 0.10 mg TP L^{-1} to a maximum of 0.17 mg TP L^{-1} for the fenced tributary and from 0.11mg TP L^{-1} to 0.18 mg TP L^{-1} for the unfenced tributary. The pattern for the fenced tributary showed a clockwise hysteresis, with concentrations decreasing on the falling limb. In contrast, TP concentrations for the unfenced tributary showed a figure-of-eight pattern, characterised by a further increase in TP concentration as discharge receded, and with the highest concentration (0.18 mg TP L^{-1}) occurring at moderate discharges (Figure 4.11a, d). For the particulate P fraction, concentration increased rapidly with discharge for both sites, indicating an initial washout of particulate material. Total P concentrations then again decreased at both sites as discharge receded, with a generally clockwise hysteresis, although it is of note that concentrations remained higher on the falling limb for the unfenced tributary than for the fenced tributary. However, the two sites again had different hysteresis patterns for SRP concentrations in this event (Figure 4.9). Interestingly, SRP concentration rose more rapidly with increasing stream discharge at the fenced tributary site, with further increases in concentration occurring on the falling limb (again a figure-of-eight pattern). Soluble reactive phosphorus concentrations at the unfenced tributary were slow to increase from baseflow to peak flow, after which they

had a clear anti-clockwise direction with highest concentrations this time coinciding with the falling limb of stream discharge (Table 4.6; Figure 4.11c, f).

No clear differences in the concentration discharge relationships was observed between the fenced and unfenced tributaries for TP, or for its two fractions, during both the June and October events in 2011 (Table 4.6; Figure 4.11g, j, h, k, i, l). The concentration-discharge relationships for TP, particulate P and SRP concentrations all displayed anti-clockwise behaviours with the higher TP, particulate P and SRP concentrations occurring on the falling limb, as the stream discharge decreased.

Table 4.6 Phosphorus concentration-discharge relationship in the fenced and unfenced tributary during four high discharge events in the Grazing period of 2010 and 2011.

Date	Parameter	Tributary	Concentration (mg L^{-1})				Stream discharge (m^3 sec^{-1})		Direction hysteresis plot
			Start	Min	Max	Cum	Min	Max	
11th – 12th July 2010	**TP**	Fenced	0.09	0.09	0.28	5.05	0.60	1.36	Figure-of-eight
		Unfenced	0.10	0.11	0.16	3.63			Clockwise
	PP	Fenced	0.06	0.13	0.19	3.81			Clockwise
		Unfenced	0.09	0.09	0.13	2.54			Clockwise
	SRP	Fenced	0.03	0.04	0.07	1.24			Figure-of-eight
		Unfenced	0.02	0.04	0.07	1.15			Clockwise
7th – 8th Sep 2010	**TP**	Fenced	0.10	0.10	0.17	3.40	6.20	12.75	Clockwise
		Unfenced	0.11	0.11	0.18	4.09			Figure-of-eight
	PP	Fenced	0.08	0.07	0.11	1.93			Clockwise
		Unfenced	0.09	0.10	0.13	2.65			Clockwise
	SRP	Fenced	0.02	0.05	0.08	1.46			Figure-of-eight
		Unfenced	0.02	0.05	0.08	1.42			Anti-clockwise
25th – 26th June 2011	**TP**	Fenced	0.03	0.03	0.16	2.01	0.31	0.46	Anti-clockwise
		Unfenced	0.10	0.04	0.11	1.72			Anti-clockwise
	PP	Fenced	0.02	0.05	0.12	1.28			Anti-clockwise
		Unfenced	0.04	0.04	0.08	0.99			Anti-clockwise
	SRP	Fenced	0.01	0.03	0.06	0.76			Anti-clockwise
		Unfenced	0.04	0.03	0.05	0.74			Anti-clockwise
2nd – 3rd Oct 2011	**TP**	Fenced	0.02	0.02	0.18	4.03	2.75	6.25	Anti-clockwise
		Unfenced	0.07	0.07	0.31	5.82			Anti-clockwise
	PP	Fenced	0.04	0.12	0.16	3.22			Anti-clockwise
		Unfenced	0.05	0.15	0.23	3.93			Anti-clockwise
	SRP	Fenced	0.02	0.08	0.11	2.08			Anti-clockwise
		Unfenced	0.02	0.07	0.09	1.96			Anti-clockwise

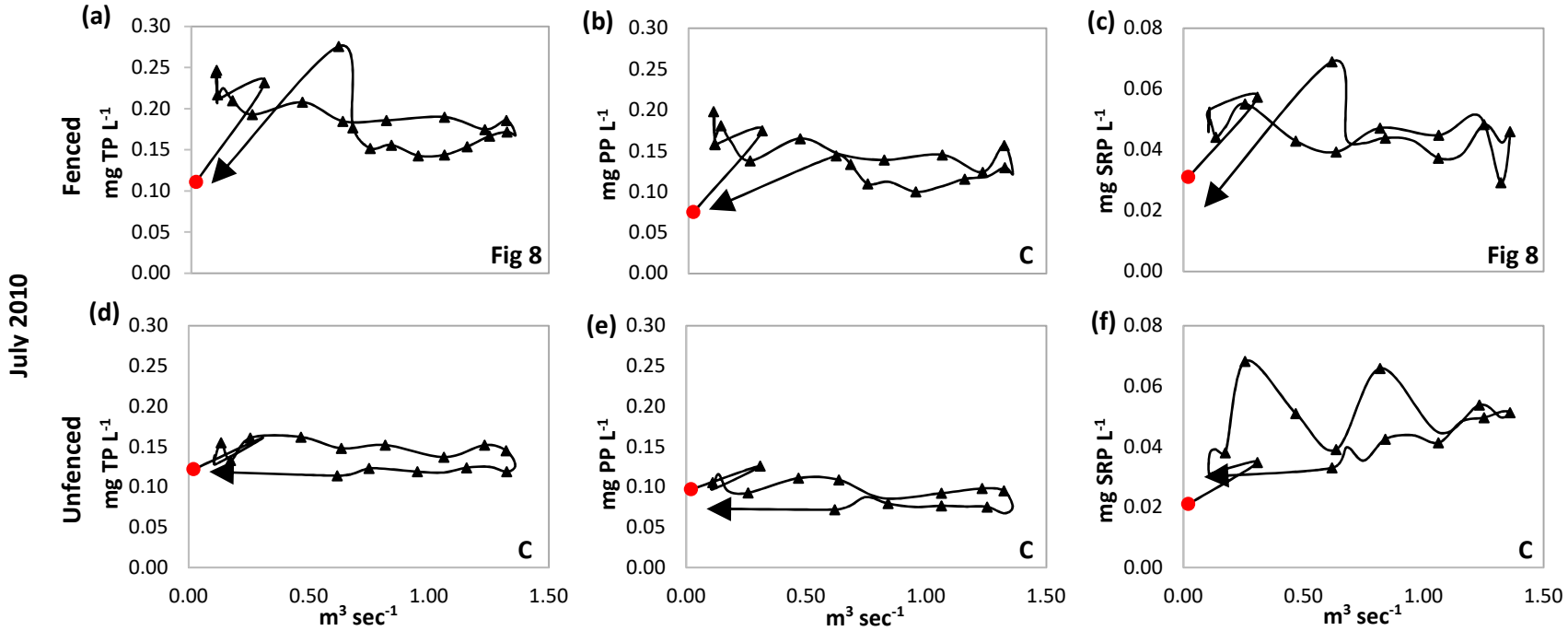

Figure 4.10 Phosphorus concentration-discharge relationships at the lower sites on the fenced and unfenced tributaries in July 2010. Red circle indicates the start of the event and the arrows indicates the direction and the end of the event. C indicates clockwise direction and Fig 8 indicates figure-of-eight direction.

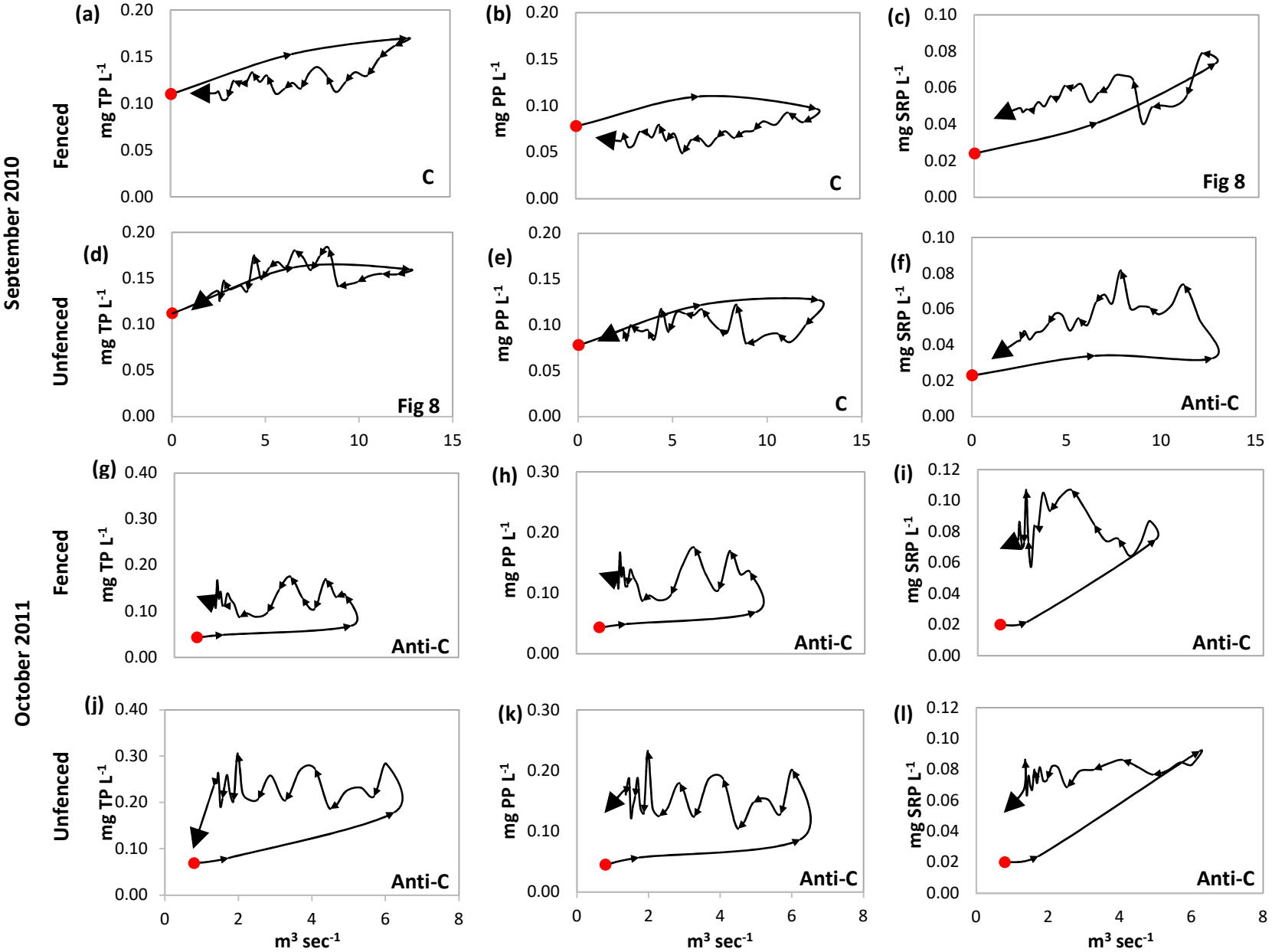

Figure 4.11 Phosphorus concentration-discharge relationships at the lower sites on the fenced and unfenced tributary during high discharge events in September 2010 and October 2011. Red circle indicates the start of the event and the arrows indicates the direction. C indicates clockwise direction, Anti-C indicates anti-clockwise direction and Fig 8 indicates figure-of-eight direction.

For TN, the fenced tributary concentration-discharge relationships displayed anti-clockwise behaviour throughout all four sampling events, indicative of slower nutrient delivery to the watercourse (Table 4.7; Figure 4.12). However, the concentration-discharge relationships for the unfenced tributary site were more variable. In mid Grazing season during the event in July 2010, both TN and TDN displayed a clockwise concentration-discharge relationship, showing a rapid washout of N at the start of the event. Total dissolved N represented 65% of TN for this event at this site. This pattern with an initial rapid increase in N concentrations was also observed for the unfenced tributary for the extreme high discharge event in September 2010, however, as the discharge weakened, higher TN and TDN concentrations were observed, giving a figure-of-eight pattern (Figure 4.12).

Similar to the P fractions, TN and TDN concentration-discharge behaviour for both sites in the June 2011 and October 2011 events showed anti-clockwise behaviour, indicating higher N washout as the stream discharge decreased (Table 4.6; Table 4.7; Figure 4.12e, g, f, h).

Table 4.7 Nitrogen concentration-discharge relationship in the fenced and unfenced tributary during four high discharge events in the Grazing period of 2010 and 2011.

Date	Parameter	Tributary	Concentration (mg L^{-1})				Stream discharge (m^3 sec^{-1})		Direction hysteresis plot
			Start	Min	Max	Cum	Min	Max	
11th – 12th July 2010	**TN**	Fenced	0.86	0.86	1.72	33.90	0.60	1.36	Anti-clockwise
		Unfenced	0.95	0.75	1.49	30.89			Clockwise
	TDN	Fenced	0.82	0.80	1.04	22.38			Anti-clockwise
		Unfenced	0.59	0.73	1.56	20.70			Clockwise
7th – 8th Sep 2010	**TN**	Fenced	0.10	0.10	3.05	68.38	6.20	12.75	Anti-clockwise
		Unfenced	1.22	1.22	4.20	78.08			Figure-of-eight
	TDN	Fenced	0.10	1.12	1.33	30.18			Anti-clockwise
		Unfenced	1.02	1.54	1.97	41.64			Clockwise
25th – 26th June 2011	**TN**	Fenced	0.76	0.51	2.99	35.91	0.31	0.46	Anti-clockwise
		Unfenced	0.94	0.26	2.26	25.33			Anti-clockwise
	TDN	Fenced	0.42	0.56	0.98	15.04			Anti-clockwise
		Unfenced	0.33	0.51	0.81	13.64			Anti-clockwise
2nd – 3rd Oct 2011	**TN**	Fenced	1.01	1.01	1.71	32.84	2.75	6.25	Anti-clockwise
		Unfenced	1.10	1.05	1.63	34.94			Anti-clockwise
	TDN	Fenced	1.01	1.48	2.41	39.83			Anti-clockwise
		Unfenced	0.80	1.91	2.97	51.68			Anti-clockwise

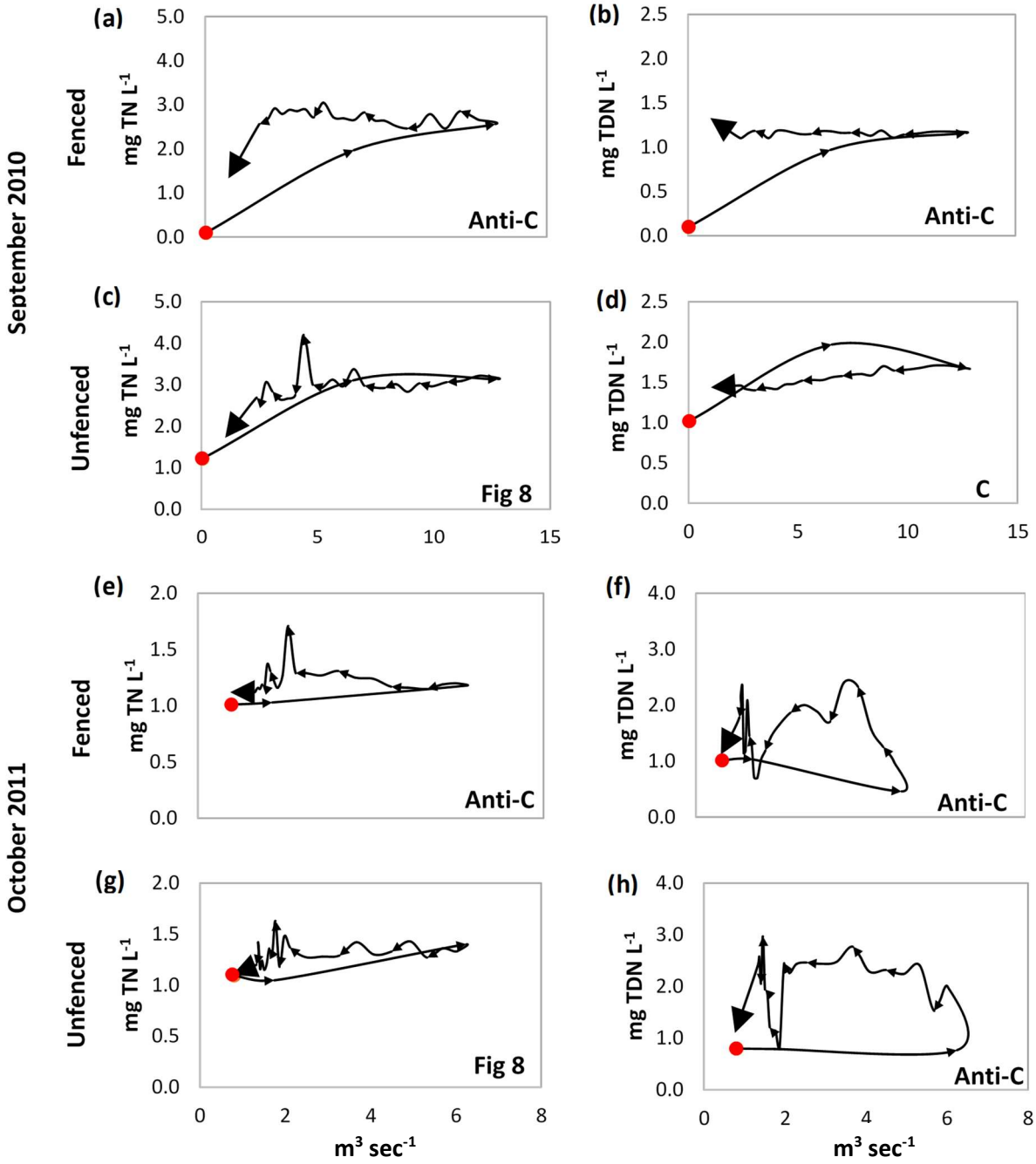

Figure 4.12 Nitrogen concentration-discharge relationships at the lower sites on the fenced and unfenced tributary during high discharge events in September 2010 and October 2011. Red circle indicates the start of the event and the arrows indicates the direction. C indicates clockwise direction, Anti-C indicates anti-clockwise direction and Fig-8 indicates figure-of-eight direction.

4.6 Discussion

Catchment riparian areas are considered key zones in which to target mitigation measures aimed at reducing the loss of nutrients from agricultural land to surface waters (Stutter et al., 2012). However, there is limited knowledge available on the evaluation of these mitigation measures, particularly in the UK and Ireland, and especially on their effectiveness at a catchment scale (Kay et al., 2009; Bergfur et al., 2012; Conroy et al., 2016). Most studies on the topic have been undertaken in the USA (Galeone, 2000; Galeone, 2006; Vidon et al., 2008; Vidon et al., 2010), Canada (Miller et al., 2010; Miller et al., 2011) and Australia (McKergow et al., 2003; Bartley et al., 2010), where agricultural practice and management approaches will differ. The main difference between agricultural practices these study catchments and those in Ireland are smaller field sizes due to different topography and Ireland being significantly smaller in size, summer grazing and winter housing due to Ireland's wetter climate, and different slurry spreading practices on agricultural land. The objective of the current study was to investigate the impact of streamside fencing, which had been installed five years earlier, on P and N concentrations in two adjacent streams. Fencing, as a mitigation measure, excludes cattle from direct access to the water and allows riparian vegetation to re-grow (Linnane et al., 2010).

Overall, this study found significant differences in the downstream concentration compared to upstream concentration, between the fenced and unfenced reaches; differences in overall concentration-discharge relationships; and differences in concentration-discharge relationships for an extreme large discharge event (Table 4.8). In particular, the results indicated that net retention of both TP and TN was occurring during the Grazing season in the fenced stream reach, while net release of both nutrients was occurring in the unfenced reach (Table 4.8). However, this relative difference between the two reaches was reversed, for TP only, during the Open season (February to April), with net release of TP from the fenced reach, and net retention of TP in the unfenced reach, suggesting that differing processes were controlling export of the two nutrients and in both reaches. There were also differing concentration-

discharge relationships for TP for both reaches during the Grazing season, and for TN during the Open slurry spreading period. In addition, the sub-daily pattern during an extreme high discharge event also differed, with the fenced site showing a clockwise pattern for TP, and a more complex figure-of-eight pattern for TN. Despite the net TP release in the fenced stream reach, the estimated annual TP and TN loads were lower for the fenced stream, representing 74% and 83% of those from the unfenced tributary respectively.

Table 4.8 Summary of chapter findings.

	Fenced	**Unfenced**
Estimated TP load	0.57 kg TP ha^{-1} yr^{-1}	0.77 kg TP ha^{-1} yr^{-1}
Estimated TN load	5.99 kg TN ha^{-1} yr^{-1}	7.24 kg TN ha^{-1} yr^{-1}
Downstream change [TP] *Grazing season* (*Apr-Oct*)	Net retention	Net release
Downstream change [TP] *Open season* (*Feb-Apr*)	Net release	Net retention
Downstream change [TN] *Grazing season* (*Apr-Oct*)	Net retention	Net release
Downstream change [TN] *Open season* (*Feb-Apr*)	Net release	Net release
Overall concentration-discharge relationship TP *Grazing season* (*Apr-Oct*)	Lower at moderate discharges; high at low and higher discharges	General increase with discharge
Overall concentration-discharge relationship TN *Open season* (*Feb-Apr*)	Lower at high discharges	General increase with discharge
Sub-daily concentration-discharge relationship TP (*Sep 2010*)	Clockwise (source close to stream)	Figure-of-eight (lagged transit time)
Sub-daily concentration-discharge relationship TN (*Sep 2010*)	Anti-clockwise (source distant from stream)	Figure-of-eight (lagged transit time)

There are several mechanisms that could contribute to the overall lower nutrient concentration and the difference in the upstream-downstream patterns in the fenced stream during the Grazing season. These include a lack of direct defecation by cattle (Miller, 2010; Bond et al., 2012), an absence of disturbance of nutrient enriched sediments by cattle (Terry et al., 2014), and the absence of areas of exposed bankside soil as found at cattle drinking sites. Cattle were excluded from the fenced stream reach, while the unfenced stream had 14 active CAPs (Table 3.1), all of which also had large areas of bare and poached soil. Bond et al. (2012) found in their study that

temperature was a key driver of when cattle entered the River Meon at Droxford in the UK. During warm dry periods, for example during the summer grazing months, cattle have a tendency to use waterways for thermoregulation (Legrand et al., 2011; Bond et al., 2012). Cattle intrusion into watercourses also results in soil poaching at the site. This can cause soil compaction, reduced soil infiltration rates and increased soil detachment rates (Conroy et al., 2016) (Figure 4.13). Furthermore, nutrient export rates from areas of bare soil, as seen close to CAPs in the unfenced reach in the Milltown Lake Catchment, tend to be higher particularly after periods of heavy rainfall (Figure 4.11) (Reichenberger et al., 2007). In addition to soil poaching, there is also a greater tendency for cattle to defecate and urinate while in the stream. Cameron et al. (2013) reported that, on average, a cow may urinate 10 to 12 times per day, which may be more frequent within waterways during warm/dry weather. Bond et al. (2012) also found in their study that cattle defecated more frequently while standing in a stream (3.2%) than in any other environment (0.6%). In addition to these cattle related pressures, higher rates of dissolved nutrient uptake by vegetation will occur during summer, while the capacity to trap particulate nutrients will also be higher in more densely vegetated buffer areas, along with a reduced discharge velocity (Dorioz et al., 2006; McConnell et al., 2013).

Figure 4.13 Cattle access points and areas of bare soil exposure along the unfenced tributary in the Milltown Lake Catchment.

All of these effects could explain the significant downstream increase in TP concentration (of which, on average, 55% was particulate P) during the Grazing season for the unfenced stream

reach, and the results of the GAM model for the overall TP concentrations in that tributary. This showed a distinct positive relationship between TP export and discharge, suggesting a washout of eroded material. In contrast, TP concentrations fell from upstream to downstream in the fenced reach and there was no clear direction in the TP concentration-discharge relationship. On this fenced tributary, cattle access and associated erosion on stream banks, was absent. However, a consistent difference between the fenced and unfenced sites was not evident in the sub-daily concentration-discharge relationships for the four individual events, highlighting the complexity of the processes involved in nutrient transfer and export.

In Ireland, grass silage harvesting for livestock winter food storage mainly occurs during the later Grazing period, with the first cut for silage generally taking place in early to mid-June (Teagasc, 2011). Slurry spreading, usually *via* the traditional broadcast (splash plate) technique, normally takes place immediately after a harvest or grazing event to minimise contamination of the grass sward (Carter et al., 2010; Mc Connell et al., 2013). High rainfall occurring after such activities will substantially increase the quantity of total P and N exported in overland discharge (Galeone, 2006; Reichenberger et al., 2007; Macintosh et al., 2011; Buckley, 2012). The vegetative buffer that had developed in the fenced reach of the Milltown Catchment over the five years since fencing, is likely to have acted as a filter to trap particulate P especially during the summer periods when vegetation cover would be higher (Figure 3.3) (Hoffmann et al., 2009). Furthermore, bioavailable P and N uptake by the vegetation within the buffer strip would have been at its highest during the growing season (Stoate et al., 2009; Roberts et al., 2012). In a study that investigated vegetative buffers similar in size to those in this study (1.5 m), Galeone (2000) found that nutrient export in overland runoff was reduced, to some extent, along streams adjacent to pastured land, with fencing consequently having a positive influence on the receiving surface water quality. Washout of slurry from adjacent fields is also likely to

have contributed to export in the unfenced reach owing to high rainfall levels, particularly as unusually high levels were recorded in Ireland in late 2011 (Oireachtas, 2011).

Interestingly, although the total rainfall for the Closed period (322 mm) was the highest of all the study periods, there was no difference in upstream to downstream nutrient behavior between the two reaches, suggesting that similar processes were driving export at this time. During winter, rainfall events become more prevalent in northern climates, while vegetation growth dies back and becomes dormant, and consequently, dissolved nutrient uptake by plants is lowest (Roberts et al., 2012). Furthermore, soils become saturated due to high rainfall, decreasing the nutrient infiltration capacity, and thus leading to increased surface runoff. Under such conditions, the vegetation within the buffer zone would be unable to filter the high influx of particulates exported in overland discharge. Such a die-off in buffer vegetation would explain the change in the upstream-downstream TP concentrations that was observed for the fenced tributary. It is likely that particulate material trapped during the summer Grazing period would then have been washed out during higher winter discharges when vegetation cover was reduced. High nutrient export in the winter months from agricultural catchments was reported, for example, in studies by Tappin et al. (2013), Bond et al. (2012) and Rozemeijer et al. (2014). Rozemeijer et al. (2014) noted in their study that nutrients exported in winter played a crucial role in summer eutrophication in downstream receiving waters.

In the study catchment and in northwest Ireland, slurry spreading is prohibited until after the 31st of January (S.I. No. 31 of 2014). Consequently, farmers may enter the early spring with significant quantities of slurry in storage tanks that must be spread on the land (Dale et al., 2012; Cameron et al., 2013). Vegetation on streambanks at this time will have died back and will only just be starting to re-establish after the winter months (Roberts et al., 2012). In the current study, during the Open period, TP (which comprised c. 55% particulate P fraction) was

released from the fenced reach, a time also when slurry spreading was again permitted. Low vegetation cover in the vegetative buffer zone (the Open period) may have resulted in the washout of additional particulate P that had previously been retained within the buffer (Hoffmann et al., 2009). A similar effect was reported by Stoate et al. (2009) who also concluded that grassy buffer strips were ineffective in retaining P during early spring, particularly after heavy rainfall events, when vegetation was underdeveloped. The Open period in the current study, had the largest sum total N concentrations, which were dominated by the dissolved nitrogen fraction (c. 75% was TDN), for both the fenced and unfenced stream reach compared to the grazing period. The high net increase in total N during this period for both stream reaches may be due, in part, to the farmers spreading slurry at this time. While vegetation growth was low, particularly in the vegetative buffer strip on streambanks during the open period, vegetation would still not play a major role in filtering the total N concentration during this period as it was dominated by the dissolved N fraction. It is of note that the relationship to discharge was distinctly different between the two reaches. While the model for the unfenced tributary showed a clear positive relationship between discharge and total N concentration, the relationship between the same parameters for the fenced tributary was less so clear.

The majority of studies to date focusing on fencing as a management option to minimise nutrient export have been carried out in Canada and the US, and they mainly investigated effects on stream total P, rather than total N. These studies, however, would have been based in areas with different agricultural and land management practices to those in Ireland, making comparison difficult. In addition, studies also have adopted a range of differing approaches, which include: upstream/downstream, pre-/post-fencing and the fenced/unfenced sampling approach, for measuring the changes in nutrient concentrations in agricultural catchment surface waterbodies. In a study of the Little Bow River, Southern Alberta, Canada, which took a similar upstream-downstream approach to the current research, Miller et al. (2010) found that

TP concentrations were similar up and downstream in a fenced stream reach over a four-year study period. Line et al. (2003), in a study with pre-and post-fencing time periods in the North Carolina Piedmont, found an overall reduction of 76% in TP concentration and a 78% reduction in TN concentration from a 14.9 ha pasture post cattle exclusion fencing. Galeone (2006) found, for an eight year study in the Mill Creek watershed, Pennsylvania, which had a similar buffer size zone (1.5 – 3.7 m) to that in the current study, a 20% reduction in total N concentration post fencing of the riverbanks. Furthermore, similar to the finding of the current study, Galeone (2006) reported that the greatest reduction in TN concentration (47%) was during the Grazing season.

Previous work carried out in the Milltown Lake Catchment has shown that the catchment has been impacted by nutrient loading from agriculture since the 1970s, with resultant eutrophication clearly evident in the lake (Carson et al., 2015). High nutrient concentrations from the unsewered rural populations in this catchment are likely to have also had water quality impacts (McCarthy et al., 2012; Rafferty, 2015), but these were found to be much lower in magnitude compared to the agricultural sources (Carson et al., 2015). The annual TP and TN loads estimated in the current study can be considered moderate when compared to studies carried out in similar catchments elsewhere in Ireland. Jordan et al. (2012) reported nutrient loads of between 0.175 - 0.785 kg TP ha^{-1} yr^{-1} and 8.9 - 28.8 kg TN ha^{-1} yr^{-1} from two intensive grassland and two arable catchments in the ROI in a study based on high frequency automated sample collection. A further study by Jordan et al. (2005) reported annual TP loads for three different Irish grassland catchments (0.2 to 88.5 km^2) of between 0.2 to 3.1 kg P ha^{-1} yr^{-1}. Furthermore, a study undertaken in a similar heavy clay drumlin catchment by Cassidy and Jordan (2011) reported annual TP loads of 1.8 kg TP ha^{-1} yr^{-1} up to 3.8 kg TP ha^{-1} yr^{-1}.

Based on the paleolimnological evidence, such moderate levels of nutrient loading can maintain eutrophic conditions and cyanobacterial blooms in Milltown Lake (Carson et al., 2015), indicating that, as with many catchments in areas with intensive cattle based agriculture in Ireland, programme of measures (POMs) that include mitigation to reduce nutrient loads are required. The reduction in nutrient loading found in the current study, particularly during the Grazing period, indicated that fencing could contribute to such measures, particularly for lakes such as Milltown Lake that have a short retention time and where autumn and winter loading will likely be washed out of the lake the following summer. Phosphorus and N loading would, therefore, be reduced during the critical time for algal blooms, i.e. in summer. However, the increase in release of P from the fenced stream reach in the period February to April found in the current study could, potentially, increase nutrient availability for early season algae in the downstream lake.

4.7 Conclusion

This study highlighted both the effectiveness and limitations of streamside fencing, and of associated narrow buffer zones, as a management tool for nutrient transfer in an intensive agricultural landscape. It indicated that such measures can be effective in TP and TN management during the Grazing period. This is the time of year when nutrient uptake by plants is at its highest and the growth of vegetation in buffer areas will be greatest. However, the results also indicated that streamside fencing is less effective in nutrient management, especially for TP, during times when vegetation in the buffer zone is reduced. The study also confirmed that the processes driving nutrient concentrations differed between the fenced and unfenced stream reaches, especially for TP. This study provides valuable information to stakeholders, policy makers, and the local community and shows how streamside fencing can be considered an effective nutrient management measure. Particularly during critical periods in the calendar year where the effects of low flow conditions and excess nutrients resulting in eutrophication are amplified.

Chapter 5: Multiple drivers of phytoplankton biomass in Milltown Lake

5.1 Abstract

Understanding the drivers of change in phytoplankton standing stock in lakes is critical for the management of water resources. While nutrient availability from either the surrounding catchment, discussed in the previous chapter, or internal lake sources play an important role in controlling the magnitude of algal blooms in lakes, local climatic factors contribute either directly or indirectly through their influence on lake biota, particularly in small lakes. A study was undertaken of the relative importance of (1). climatic factors and (2). nutrient availability in controlling phytoplankton biomass in Milltown Lake, County Monaghan, at five depths between the surface and lake bottom. This chapter used the Lake Analyzer programme to calculate a set of metrics describing the physical structure of Milltown Lake using temperature sensor data, to get a better understanding of the lakes seasonal thermal mixing regime. The principal drivers of change in Chl-*a* were investigated using a General Additive Model approach. The sampling period (April to September 2012) was characterised by high rainfall and nutrient loading throughout the summer, with lake TP concentrations remaining above 0.042 mg TP L^{-1}. The analysis found that, under these high nutrient conditions, climate-related factors were the main drivers of change in Chl-*a* at all depths. However, different climatic forcing factors operated at the surface (wind speed and inflow discharge rate), compared to the lower sampling depths (thermocline depth and PAR). The only significant relationship with nutrient concentration was with in-lake NH_4-N at the lower depths. These results highlighted the sensitivity of phytoplankton biomass in small eutrophic lakes to current and future climatic change.

5.2 Introduction

Globally, the environment is changing at an unprecedented rate, with temperature and precipitation having altered dramatically already and predicted to change even more

(Christensen et al., 2007; Meehl et al., 2007). These changes may bring about changes in other environmental conditions, such as nutrient loading and water column mixing, making it a challenge to assess the drivers of Chl-*a* in a lake's ecosystem (de Senerpont Domis et al., 2013). The climate change effects on lakes that have received most attention have been those related to warming, with the effects predicted to be substantial (Havens et al., 2016). An example of this is seen in the comparison made by Jackson et al. (2007) between lakes in Denmark, where winter air temperatures tend to stay above 0 ^{o}C, and lakes in Canada, where winter air temperatures fall below -10 ^{o}C and there is ice cover on the lakes. Jackson et al. (2007) found that the Danish lakes had a fourfold higher ratio of Chl-*a* to TP, and a stronger relationship between the biomass of zooplankton to phytoplankton than the Canadian lakes. Further studies by Kosten et al. (2012) showed that the comparison of phytoplankton community structure data from lakes along a latitude gradient from northern Europe to the tip of South America indicated that percentage dominance of cyanobacteria increased steeply with increasing temperature.

In addition to temperature changes, a change in the intensity and annual distribution of rainfall is also projected for some regions (Wentz et al., 2007; Nolan et al., 2010; Jennings et al., 2009). Such changes will likely result in increased nutrient loading, and changes in the pattern of loading to lakes from the surrounding catchment, especially if high rainfall events occur more frequently during summer. Nutrient enrichment of freshwater lakes in Ireland is predominantly attributed to incidental losses from agriculture in the surrounding watershed during periods of wetter weather (Jordan et al., 2005). The pattern in loading has also been projected to change in the future in response to changes in rainfall patterns (Jennings et al., 2009), with consequent changes in Chl-*a* in lakes (Dalton et al., 2016). Overall, global climate warming will have major implications for freshwater ecosystems and may cause a seasonal shift (Dalton et al., 2016), alter the incidence of harmful algal blooms and lead to

changes in ecosystem biodiversity (Sommer et al., 2012). Furthermore, Blenckner et al. (2007) predicted that, under future climate change scenarios, a change in phenology or increase in invasive species may occur.

The composition of phytoplankton communities in lakes, and therefore the total standing stock of phytoplankton, is controlled by site specific factors, including local meteorological conditions and nutrient availability (Cloern and Jessby, 2010). The link between the level of nutrient enrichment and phytoplankton and benthic biomass is well understood for lakes (Canfield and Hodgeson, 1983; Vollenweider, 1989). The reduction of nutrients, and of P concentrations in particular, is seen as a key requirement to achieve good ecological status within waterbodies (Bowes et al., 2012). Reynolds (2002), however, stated that external forcing or disturbances are also key drivers of changes in phytoplankton assemblages. Disturbance effects on changes in phytoplankton species succession and biomass may be directly correlated with environmental stressors, for instance phytoplankton bloom formation may be influenced by thermal structure and mixing regime within a lake (Paerl and Paul, 2012). Furthermore, Mortensen et al. (1994) identified shallow lakes, in particular, as being more easily influenced by fluctuations in the physical environment caused by climatic factors such as temperature, wind, and light. As suggested by Blenckner et al. (2007), it is these local weather conditions which govern many of the physical aspects of lakes ecosystems and therefore, either directly or indirectly influence lake biota. This chapter first reviews the known effects of climate and nutrients on phytoplankton standing stock and then presents results for a case study over one growing season in 2012.

5.3 Aims

Previous work carried out in the Milltown Lake Catchment used paleolimnological techniques to examine the historical drivers of nutrient enrichment and in-lake biological responses

(Carson et al., 2015). Carson et al. (2015) found that the indicators of overall algal abundance were significantly related to both sedimentary P levels and P losses to water from the catchment, with agricultural intensification being the main contributor to increases in nutrient loading between 1970 and 2008 in Milltown Lake. Building on these findings, the work presented in this chapter aimed to investigate the relative importance of (1). local weather changes and their effects on lake physical characteristics, including stratification, and (2). nutrient (P and N) levels on the standing stock of phytoplankton biomass as measured by Chl-*a*. To put the data from the study year (2012) into context, climate and lake thermal regime data are also presented for the two preceding years: 2010 and 2011.

5.4 Material and methods

Meteorological data were obtained from the Ballyhaise and Coose Met Éireann weather stations, while high frequency stream discharge data were obtained from the EPA staff gauge on the Drumleek River (Figure 3.1; Figure 3.4). High resolution lake temperature and DO data used in this chapter were obtained from *in-situ* lake Tidbit sensors and D-Opto sensors, respectively (Section 3.5). Analytical methods for nutrients and Chl-*a* analysis used in this chapter for monitoring at the lake inflow, and at the deepest point in Milltown Lake, are described in Sections 3.4 and 3.6 (Figure 3.1).

5.4.1 Examining the inter-annual thermal structure using Lake Analyzer

The changes in lake physical structure were examined from the 16th of April 2010 until the 31st of December 2012 using high resolution lake temperature data (Section 3.5). Schmidt stability, buoyancy frequency, Wn and thermocline depth were determined from vertical temperature profiles and wind speed data using Lake Analyzer (Read et al., 2011) (Section 3.7). Thermocline depth calculations excluded the uppermost 0.5 m of the water column due to

diurnal surface water heating which at times created a strong but short-lived (sub-daily) density gradients (Simmonds et al., 2015).

5.4.2 Sampling programme assessing the importance of both climatic stressors and nutrient availability in controlling the standing stock of phytoplankton biomass

Lake water samples were collected at a range of depths on 16 occasions between the 1st of May 2012 and the 17th of September 2012 at the deepest point of the lake (~10 m) (Figure 3.1b). These were collected on a fortnightly basis during the spring (1st of May 2012 to 31st of May 2012) and autumn (4th of September 2012 to 17th of September 2012) and on a weekly basis during the remaining sampling period. It was decided to focus on weekly sampling during the summer months, as stratification for Milltown Lake had occurred during this period in the previous two years. Samples for nutrients analysis were collected at the sampling point using an Eijkelkamp® peristaltic pump with pre-measured 1 m interval tubing, at approximately 1 m depth intervals (0.1, 1, 2, 3, 4, 5, 6, 7, 8 and 9 m). In addition, samples for Chl-*a* analysis were collected at the surface and at approximately 2 m depth intervals (i.e. at 0.1, 2, 4, 6 and 8 m) at the same location. All water samples (nutrient and Chl-*a*) were collected using 2 L pre-acid washed polyethylene bottles, rinsed with ultrapure water. Sample bottles were rinsed with lake water from the depth to be sampled prior to sample collection. Methods used for the analysis of total nutrients, dissolved nutrients and Chl-*a* are described in Chapter 3. Additional lake measurements on each occasion included transparency using a Secchi disk, DO concentration and temperature, using a YSI 556 MPS multi probe (with a 30 m extension) to verify the *in-situ* sensor data. The portable YSI probe (YSI 556 MPS multi probe with a 30 m extension) was calibrated in the laboratory prior to carrying out field work and assessed periodically throughout the sampling trip. Depth at the sampling point on the day of sample collection was measured using a handheld Hondex (PS-7) Portable Depth Sounder.

An autosampler (HACH® Sigma 900 Max) was placed at the same location as the EPA staff gauge on the Drumleek River, 500 m upstream of the only lake inflow. This autosampler was set to collect composite daily water samples for TP and TN analysis for the same time period (1st of May 2012 to 17th of September 2012) (Figure 3.1a). The sampler was programmed to collect six 50 ml samples per day at 4 hour intervals, giving a final daily sample volume of 300 ml. The polyethylene sample bottles were pre-acid washed and rinsed with Milli-Q water. Sample bottles were collected on the same days as the lake samples. Stream discharge data from an EPA managed staff gauge provided continuous stream discharge data.

5.4.3 Data analysis

Discharge and meteorological data were obtained from the Ballyhaise and Coose Met Éireann weather stations and were available for all 137 days of the 2012 sampling period (1st May to the 17th of September 2012) (Figure 3.1; Figure 3.4). Photosynthetically Active Radiation (μE m^{-1} sec^{-2}) measurements were estimated from hourly shortwave radiation (SW) (Wm^{-2}) from the Ballyhaise Met Éireann weather station by multiplying the SW radiation by 0.45 (Pinker et al., 2010). Daily nutrient loads were calculated for the catchment at the inflow site as the product of concentration and 137 estimated daily flows and expressed in g ha^{-1} day^{-1}. Statistical analyses were carried out using the R statistical package version 3.2.2 (R 195 Core Team, 2015). General additive modelling was used to identify the main drivers of estimated Chl-*a* concentrations. Analysis was carried out using the mgcv package (Wood, 2006) in R (version 3.2.5, R 195 Core Team, 2015). The spreads of the residuals were relatively homogenous, indicating that a Gaussian distribution was appropriate for the model (Zuur et al., 2009). All data sets were assessed for any breaches of the assumptions of independence and heteroscedasticity using the methods in Zuur et al. (2009). All data sets conformed to these assumptions.

5.5 Results

5.5.1 Meteorological and hydrology data

The study catchment had relatively mild and wet conditions for the years 2010-2012, typical of weather conditions in the east of Ireland (Figure 5.1). Overall, the mean annual air temperature was 8.0 ºC in 2010, 9.6 ºC in 2011 and 9.2 ºC in 2012. Total rainfall in these three years were 1017 mm $year^{-1}$ (2010), 1045 mm $year^{-1}$ (2011) and 1059 $year^{-1}$ (2012), respectively. The highest number of wet days (184 days) were recorded in 2012, with 2010 having 145 wet days and 2011, 177 wet days. Average daily rainfall was also highest (2.90 mm day^{-1}) in 2012 compared to the previous two years (2.78 mm day^{-1} in 2010 and 2.86 mm day^{-1} in 2011), coinciding with the highest average stream discharge of 2.90 m^3 sec^{-1} (2012). Average discharge recorded in 2010 and 2011 were 2.78 m^3 sec^{-1} and 2.86 m^3 sec^{-1}, respectively.

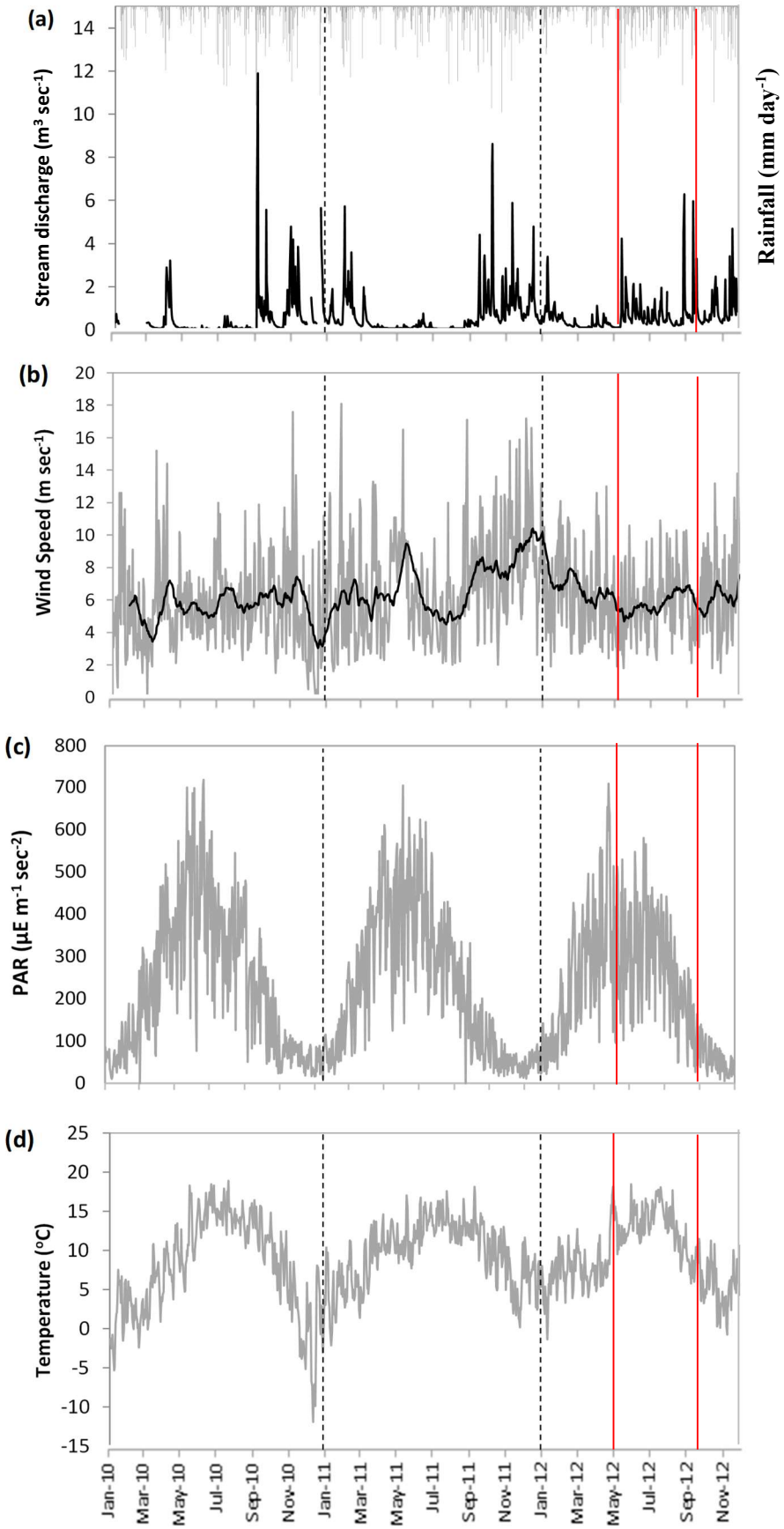

Figure 5.1 2010 to 2012 data for **(a)** daily rainfall (mm day^{-1}) at Coose Met Éireann weather station, plotted against daily stream discharge (m^3 sec^{-1}) for the EPA staff gauge site on the Drumleek River, **(b)** daily average wind speed and 30 day moving average wind speed (black line) for Milltown Lake, **(c),** daily average photosynthetically active radiation (PAR) and **(d)** daily mean air temperature (°C) at Ballyhaise Met Éireann weather station, between 1st of January 2010 and 31st of December 2012. The dotted black lines define each calendar year, while the area between the solid red lines define the sampling period in 2012.

The mean daily air temperatures recorded were similar in the period of the lake Chl-*a* study (1st of May to the 17th of September 2012) to the same time frame for the two preceding years. Overall the highest mean daily air temperature between the 1st of May to the 17th of September, at the Ballyhaise weather station was recorded in 2010 (13.5 ºC), while mean daily air temperatures for the same period in 2011 and 2012 were both lower with 12.4 ºC and 12.3 ºC respectively (Table 5.1). Maximum air temperatures recorded for the equivalent study months in 2010 (on 21st of June 2010) and 2012 (on 26th of May 2012) were both 18.3 ºC, while in 2011 the maximum air temperature reached 17.0 ºC on the 03rd of June 2011 (Figure 5.1d; Figure 5.2d). The mean daily wind speed from the 1st of May to the 17th of September in 2010 was 5.2 m sec^{-1}, with the highest daily wind speed (9.7 m sec^{-1}) occurring on the 7th of July 2010 (Table 5.1; Figure 5.1b). Mean daily wind speed during the same period in 2011 was 6.6 m sec^{-1}, with the highest daily wind speed (13.1 m sec^{-1}) occurring on the 23rd of May 2011 (Table 5.1; Figure 5.1b). In 2012, the mean daily wind speed was lower at 5.5 m sec^{-1}, while the highest daily wind speed of 10.8 m sec^{-1} was recorded on the 14th of May (Table 5.1; Figure 5.1b; Figure 5.2b). Surface PAR, as might be expected, showed a similar trend as air temperature, increasing in the spring and summer months and decreasing in the autumn and winter months (Figure 5.1c, d). During the study period equivalent months in 2010, the maximum daily mean PAR was 717 µE m^{-1} sec^{-2} on the 21st of June 2010, while the minimum of 76 µE m^{-1} sec^{-2} was recorded on the 9th of June 2010 (Table 5.1; Figure 5.1c). Maximum daily mean PAR for 2011 and 2012 were 704 µE m^{-1} sec^{-2} (3rd of June 2011) and 653 µE m^{-1} sec^{-2} (26th of May 2012), while the minimum PAR recorded for the same years were 125 µE m^{-1} sec^{-2} (16th of May 2011) and 95 µE m^{-1} sec^{-2} (8th of June 2012) respectively (Table 5.1; Figure 5.1c; Figure 5.2c).

Notably, total rainfall at Coose weather station for the study period was almost double that for 2010 and 2011 (Table 5.1). In those years, it was 264 and 226 mm respectively, while in 2012 it was 479 mm. The mean daily rainfall during the same period ranged was 2.9 and 2.5 mm day-

^{1} in 2010 and 2011, and 3.5 mm day^{-1} in 2012 (Table 5.1). Maximum rainfall of 27.5 mm day^{-1} was recorded on the 8th of June 2012 (Table 5.1; Figure 5.1a; Figure 5.2a). The wettest year (days ≥ 1 mm of rain) was again 2012 with 174 wet days, while 2010 was the driest (137 wet days) (Figure 5.1a; Figure 5.2a). Daily stream discharge at the EPA staff gauge on the Drumleek River over the three years (2010, 2011 and 2012) reflected these differences in rainfall. The maximum daily value was 12.1 m^{3} sec^{-1} on the 6th of September 2010 (Figure 5.1a). The mean daily stream discharge was 0.45 m^{3} sec^{-1} in 2012 (Table 5.1; Figure 5.2a).

Table 5.1 Comparative summary table of meteorological data (Ballyhaise and Coose Met Éireann weather station) and hydrological data (EPA staff gauge) during the study period months (1st May to the 17th of September 2012) for the same period in the previous years 2010 and 2011.

1st May to the 17th of September	**2010**	**2011**	**2012**
Mean daily air temp (Ballyhaise) (^{o}C)	13.5	12.4	12.3
Mean daily wind speed (Ballyhaise) (m sec^{-1})	5.2	6.6	5.5
Max PAR (µE m^{-1} sec^{-2})	717	704	653
Min PAR (µE m^{-1} sec^{-2})	76	125	95
Mean daily rainfall (Coose) (mm day^{-1})	2.9	2.5	3.5
Cumulative rainfall (Coose) (mm y^{-1})	264	226	479
Max daily rainfall (Coose) (mm day^{-1})	24.6	15.9	27.5
Mean daily stream discharge (m^{3} sec^{-1})	0.08	0.13	0.45

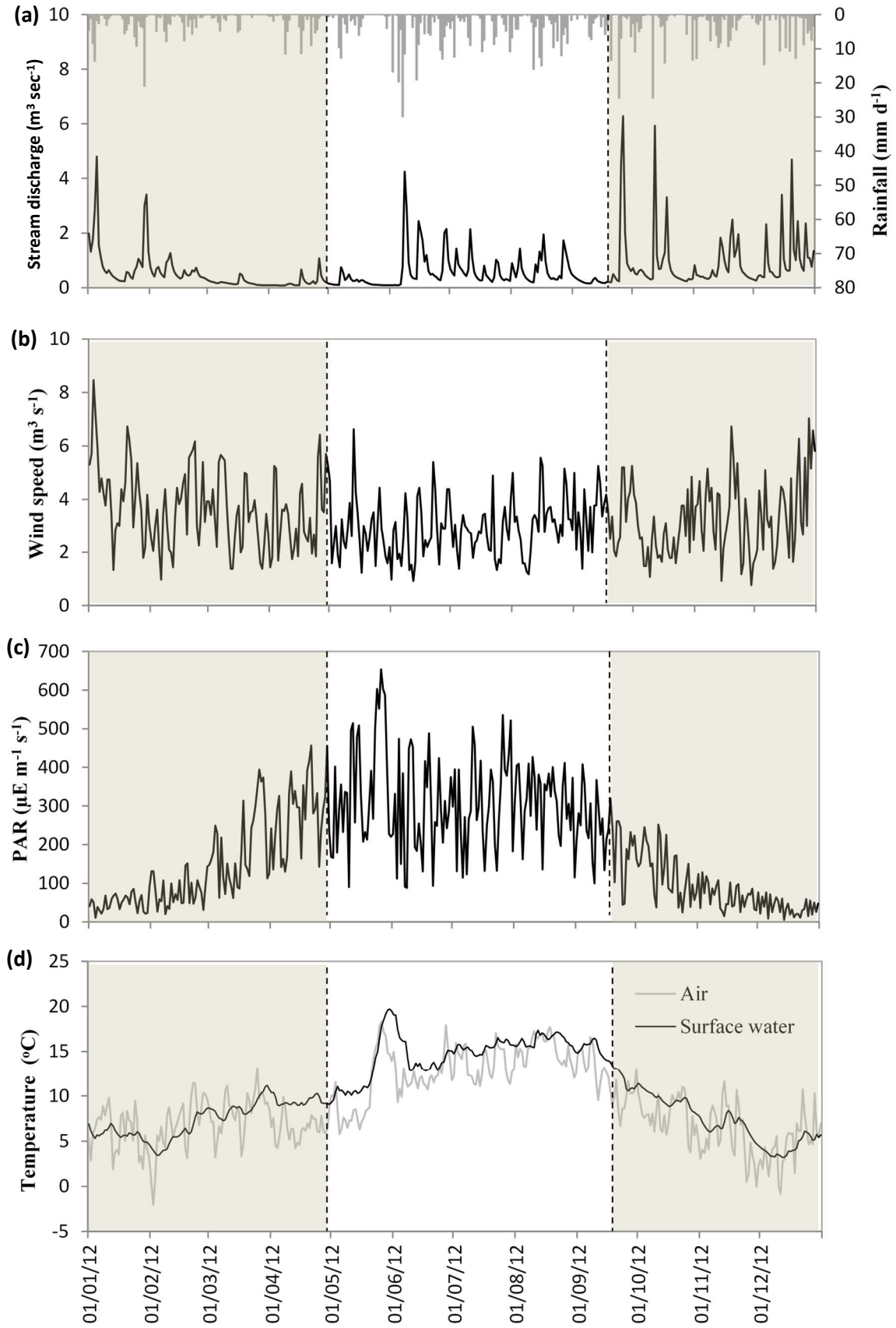

Figure 5.2 2012 data for **(a)** daily rainfall (mm day^{-1}) at Coose Met Éireann weather station, plotted against stream discharge (m^3 sec^{-1}) for the EPA staff gauge site on the Drumleek River, **(b)** daily average wind speed and 30 day moving average wind speed (black line) for Milltown Lake, **(c)** daily average photosynthetically active radiation (PAR) from the Ballyhaise Met Éireann weather station and **(d)** daily average surface water temperature for Milltown Lake and air temperature from the Ballyhaise Met Éireann weather station, January to December 2012. The white area between the dashed lines represents the study period (1st May to the 17th of September 2012).

5.5.2 Annual lake temperature and stratification profile (2010, 2011 and 2012)

While Milltown Lake generally displayed monomictic behaviour, there were also periods of mixing and re-stratification during summer in each of the years 2010, 2011 and 2012, and differing pattern in other metrics of lake physics in each year (Figure 5.3a). Higher wind speeds often resulted in the lake becoming mixed. In 2010, Milltown Lake stratified on the 28th of April 2010 and generally remained stratified, with high stability, until particularly high wind speeds (maximum wind speed reaching 11.5 m^3 sec^{-1}) on the 30th of October 2010 when the lake became fully mixed (Figure 5.1b; Figure 5.3a). In 2011, in contrast, the lake initially stratified on the 17th of March. Throughout the spring and summer, the lake went through numerous short stratification and mixing processes. There was a notable period of intense stratification and high stability in 2012, starting on the 21st of May which lasted until the 08th of June (Figure 5.3a; Figure 5.4c). It then continued to stratify for short periods until it became fully mixed on the 15th of September 2012.

In 2010, S and buoyancy frequency increased from 07th of April 2010 and remained high over the stratification period (Figure 5.3a, b, c). Values of S ranged from 8.6 J m^{-2} to a maximum of 83.8 J m^{-2} and N ranged from 0.0007 N s^{-1} to 0.0068 N s^{-1} (07th April to the 02nd of July 2010). Milltown Lake remained stable and fully stratified until a breakdown in stratification occurred after the 30th of October 2010 and the lake became fully mixed once more. Overall, the strongest vertical stratification was seen in 2010 when the Wn reached 52.1 Wn, on the 21st of December (wind speed reached 4.6 m^3 sec^{-1}) when the lake experienced a brief period of isothermal stratification (Figure 5.3d). Average temperatures above the thermocline were 1.3 °C and below the thermocline 3.1 °C during this period. In 2011, however, S and N did not have the same consistent pattern as in 2010. Both initially increased from the 22nd of February until the 30th of April 2011 to 33.6 J m^{-2} and 0.003 N s^{-1} respectively, when there was sudden decrease from the 30th of April until the 26th of May 2011. There was a build-up in lake stability from the 30th of

May until the 05th of August 2011 with a maximum stability of 40.2 J m^{-2}, Wn on the same day was 29.3 Wn. Breakdown in stability occurred on the 16th of October 2011. Both S and N increased again on the 21st of May 2012 and peaked at 50.3 J m^{-2} and 0.006 N s^{-1} respectively on the 30th of May 2012 (Figure 5.3b, c).

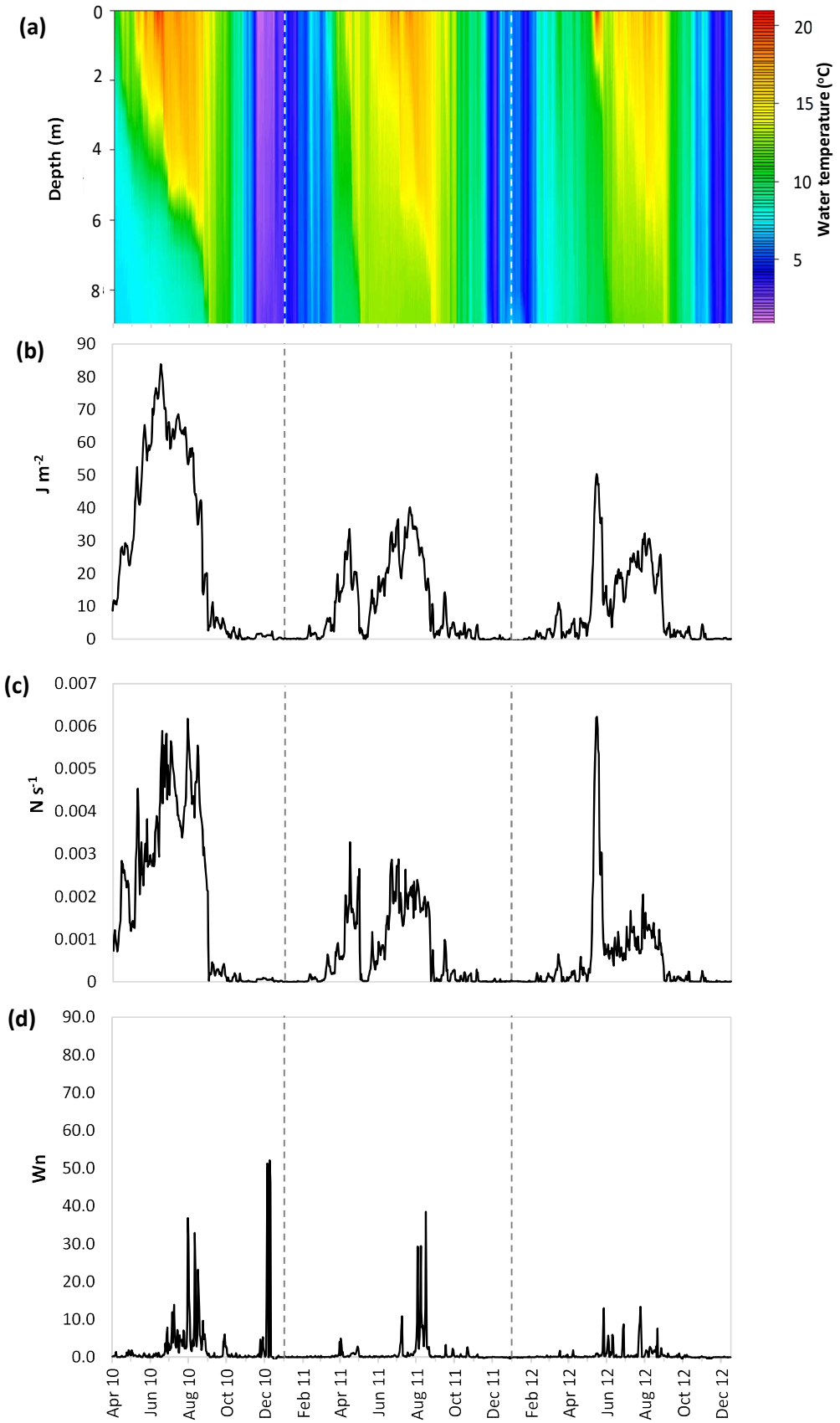

Figure 5.3 16th of April 2010 and the 31st of December 2012 **(a)** contour plot of lake water temperature (°C), **(b)** Schmidt stability (J m^{-2}), **(c)** buoyancy frequency (N s^{-1}) and **(d)** Wedderburn number (Wn). The dotted grey lines define each calendar year.

5.5.3 Lake abiotic data (01st of May to the 17th of September 2012)

Mean daily TP loads from the Milltown Lake Catchment at the inflow to Milltown Lake in the study period (1st of May to the 17th of September 2012) were relatively high for summer, at 1.6 g P ha^{-1} d^{-1}, while the mean total N export was 22.0 g N ha^{-1} d^{-1}. The maximum total P (28.3 g P ha^{-1} d^{-1}) and total N (277.9 g N ha^{-1} d^{-1}) loads were recorded on the 8th of June 2012, coinciding with the maximum rainfall and stream discharge (Figure 5.4a). This peak was followed by consistent pulses in P and N loading for the rest of the summer, reflecting the peaks in river discharge.

During the more intense stratification period from 21st of May until 8th of June (19 days), the surface mixed layer depth ranged between 1 m and then progressively increased to a maximum depth of 3.6 m on the 8th of June 2012. The mean Secchi depth reading during this period was 1.5 m. The surface mixed layer temperatures ranged from 12.1 ºC (21st of May) to 19.7 ºC (30th of May). Temperatures below the thermocline had a lower range, from 9.7 ºC to 10.3 ºC. The hypolimnetic water started to become anoxic during this period of stratification (Figure 5.4b). The average DO above the thermocline was 8.91 mg L^{-1} while that below the thermocline was 5.75 mg L^{-1} (Figure 5.4b). The mean S was 36.1 J m^{-2} and included the maximum S level for the overall sampling period (50.4 J m^{-2}) on the 30th of May 2012 (Figure 5.4d). However, the lake then mixed to 7.7 m immediately after the high rainfall on 8th of June and a concurrent decrease in air temperature from 13.9 ºC to 11.0 ºC, and remained fully mixed until 16th of July 2012. Secchi depth on the 8th of June measured 0.97 m and maintained an average depth of 0.95 m until the lake began to stratify again on the 16th of July 2012.

Between, the 16th of July and the 25th of August 2012, stratification was again established but was weaker than in late May/early June and followed a deepening trend as the summer progressed. This time period included several shorter periods where the mixed surface layer depth was shallow (ranging between 1.0 m to 2.3 m) which only lasted between 3 to 7 days. A

period with slightly more intense stratification occurred between the 11th of August and the 25th of August 2012 (15 days), with the thermocline depth ranging between 2.0 m (11th of August) and 6.1 m (18th of August). The mean Secchi depth between this stratified period measured 0.9 m on the 12th August 2012. During this stratified period, the mean water temperature for the surface mixed layer was 15.6 ºC, while the mean water temperature beneath the thermocline depth was 13.0 ºC. The mean DO during this period (11th of August to the 18th of August 2012), above and below the thermocline were 6.81 mg L^{-1} and 0.99 mg L^{-1} respectively (Figure 5.4b). The lake became isothermal again on the 15th of September 2012 (Figure 5.4c).

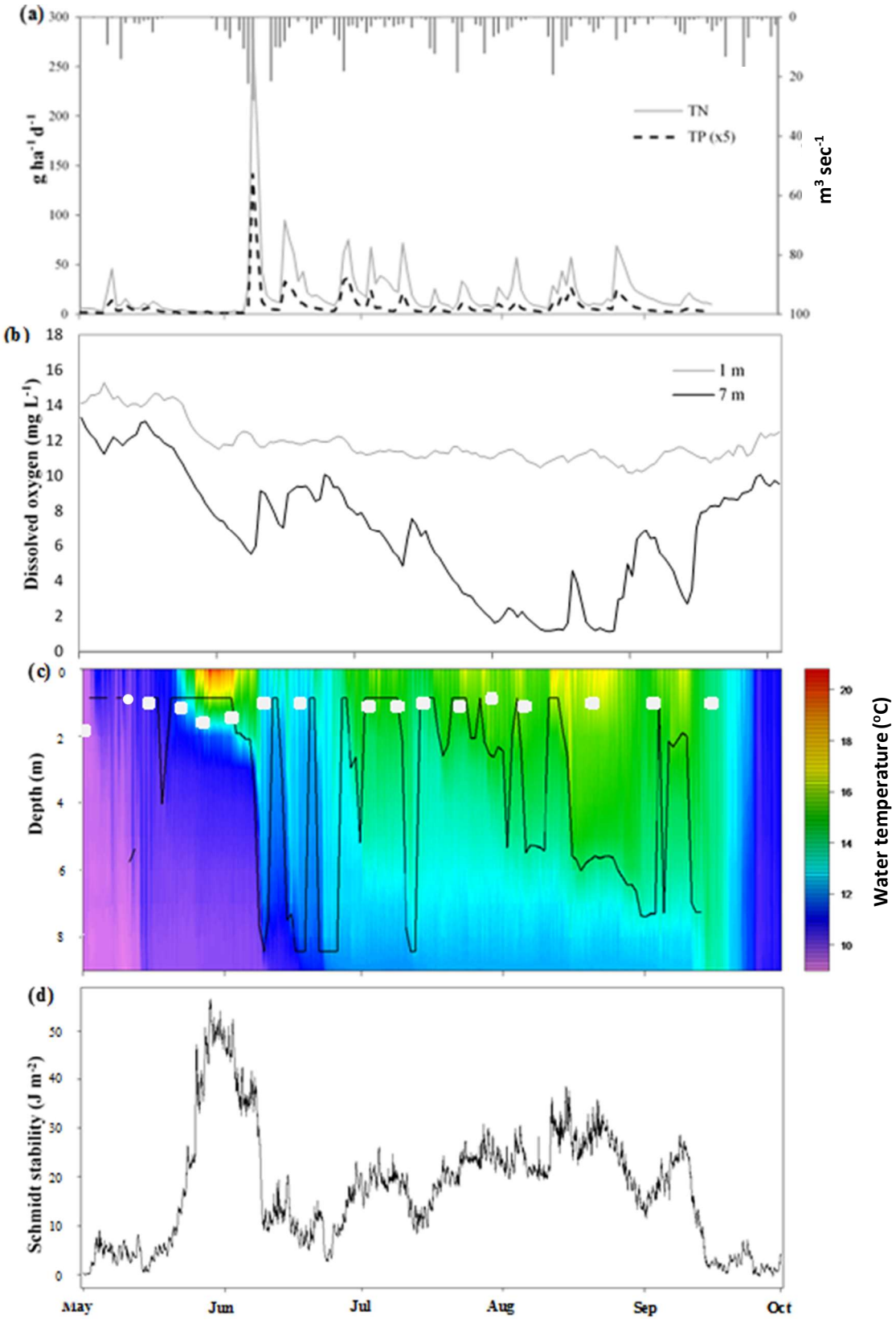

Figure 5.4 1st of May to the 1st of October 2012, **(a)** stream discharge (m^3 sec^{-1}) and nutrient loadings (g ha^{-1} d^{-1}) from the lake inlet site, **(b)** dissolved oxygen (mg L^{-1}) at 1 m and 7 m depth **(c)** contour plot of lake temperature (°C) with thermocline depth (m) (superimposed black line), Secchi depth measurement on day of sampling (m) (superimposed white dots) and **(d)** Schmidt stability (J m^{-2}). Note difference in scale for total N and total P loads.

The maximum Chl-*a* levels (44.5 µg L^{-1} at the surface) were actually recorded at the start of the study period on the 17th of May 2012, with high concentrations (mean 31.2 µg L^{-1}, n = 5) occurring throughout the water column on this date (Figure 5.5a). Immediately following the onset of the period of intense stratification in late May, concentrations at the surface actually reduced to 9.0 µg L^{-1} (on the 24th of May). However, it was also notable that during the initial days of intense stratification, Chl-*a* levels were higher below the shallow 1.0 m thermocline depth, with concentrations of 32.8 µg L^{-1} and 9.5 µg L^{-1} measured at the 2 m sampling depth on 24th of May and 29th of May, respectively. In contrast, surface Chl-*a* concentrations on these days were 9.0 µg L^{-1} and 4.7 µg L^{-1}. This pattern changed toward the end of that stratification period as the thermocline depth increased to a maximum of 3.6 m on the 8th of June 2012, when a higher Chl-*a* concentration was again recorded in the surface (0.1 m) layer (mean Chl-*a* 17.3 µg L^{-1}) than in the deeper layers (Chl-*a* range: 2.7 µg L^{-1} at 8 m to 7.5 µg L^{-1} at 4 m). A further peak in Chl-*a* concentrations occurred around the 31st of July 2012 (Figure 5.5a). However, again, the maximum levels of 27.2 µg L^{-1} were detected at the 4 m depth, which was below the thermocline depth of 2.4 m.

Phosphorus concentrations in the lake itself ranged between 0.042 and 0.149 mg P L^{-1} for TP and 0.017 and 0.084 mg P L^{-1} for SRP. High concentrations of TP (mean 0.088 mg P L^{-1}) were recorded in the upper layers (thermocline depth ranging between 1.0 m to 5.8 m) in the two weeks prior to stratification on the 21st of May 2012 (Figure 5.5b). However, concentrations gradually decreased throughout the water column once stratification had started, with a minimum of 0.043 mg P L^{-1} on the 4th of June (Figure 5.5b). Total P concentrations increased after this stratification period at all depths (8th of June) and remained consistently high (> 0.556 mg P L^{-1}) until the 4th of September (Figure 5.5b). Throughout late July and early August, TP concentrations were generally found to be higher above the thermocline depth (2.8 m) than below it. However, high TP concentrations were observed below the thermocline on both the

16th of July (0.142 mg P L^{-1}) and 31st of July (0.148 mg P L^{-1}). During the period with most intense stratification (21st of May to the 8th of June 2012), high concentrations of SRP were observed below 6 m, ranging between 0.028 mg P L^{-1} and 0.043 mg P L^{-1} (Figure 5.5c). During July, increased SRP concentrations were found throughout the water column on two separate occasions, a mean of 0.053 mg P L^{-1} on the 4th of July and a mean of 0.059 mg P L^{-1} on the 24th of July (Figure 5.5c). Once the lake became isothermal on the 15th of September 2012, the mean TP and SRP concentrations recorded were 0.042 mg TP L^{-1} and 0.024 mg SRP L^{-1}, respectively.

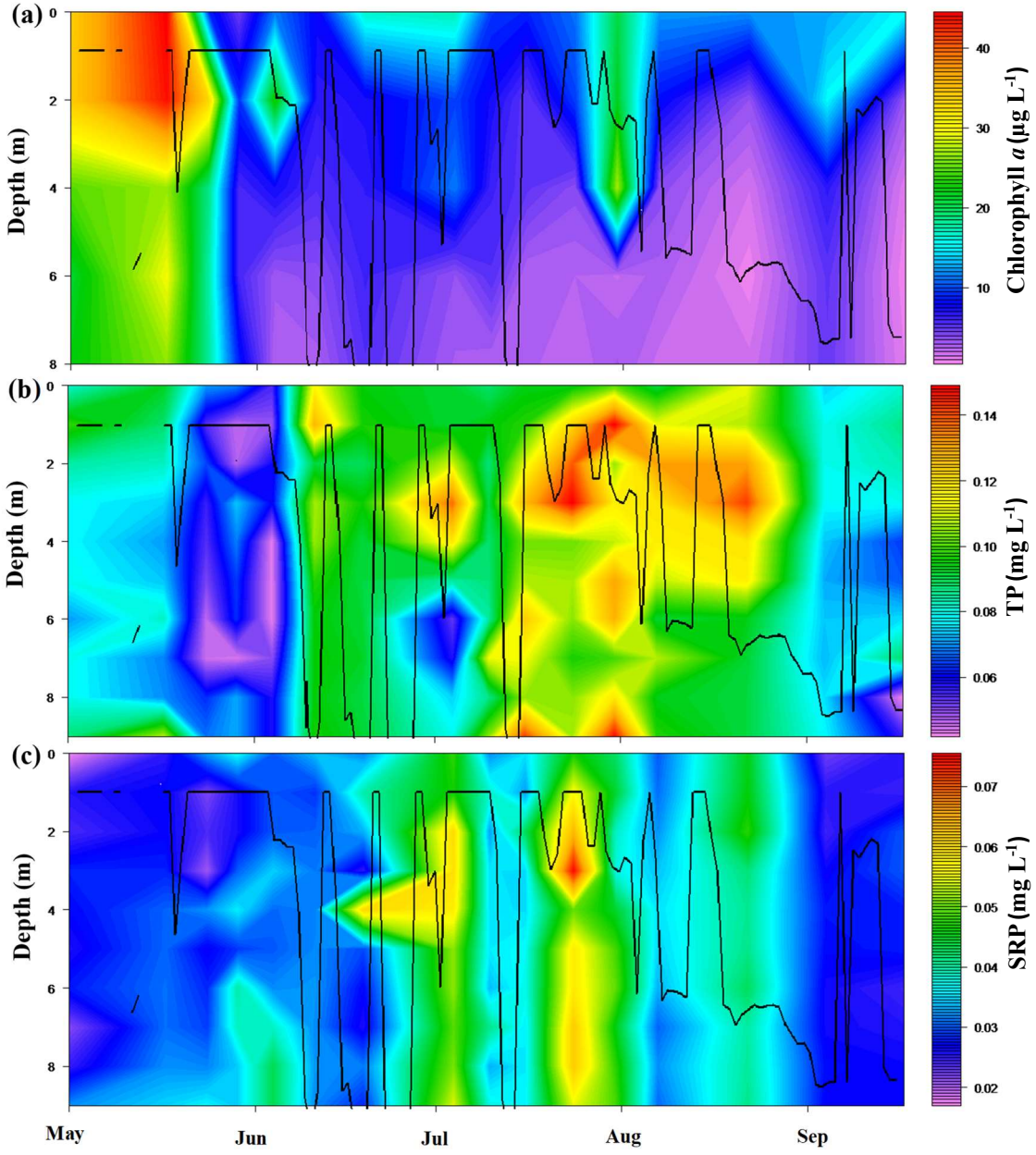

Figure 5.5 Contour plots of **(a)** chlorophyll *a* (µg L^{-1}), **(b)** TP (mg L^{-1}) and **(c)** soluble reactive phosphorus (SRP) (mg L^{-1}), with thermocline depth superimposed (m), at the deepest point in Milltown Lake, between the 1st of May 2012 and the 17th of September 2012.

During the months of May and June, total N concentrations were always less than 2 mg N L^{-1}, but increased throughout the water column from July onwards, with maximum concentrations of 4.6 mg N L^{-1} (≤ 1 m) on the 24th of July 2012 (Figure 5.6a). For the two weeks prior to stratification on the 21st of May, NO_3-N concentrations were high throughout the water column (between 0.65 mg N L^{-1} and 0.88 mg N L^{-1}). During the stratified period (21st of May to the 08th of June 2012), NO_3-N concentrations decreased to a water column mean of 0.44 mg NO_3-N L^{-1}. Concentrations of NO_3-N increased on the 11th of June (mean 0.79 mg N L^{-1}) but decreased by the 19th of June (mean 0.44 mg -N L^{-1}) (Figure 5.6c). On the 4th of July 2012 at the 3 m depth interval, concentrations of NO_3-N spiked to 0.92 mg N L^{-1}. While concentrations remained high until the 7th of August, NO_3-N levels reached further highs with an average of 0.78 mg N L^{-1}, throughout the water column until the end of the sampling period (17th of September 2012) (Figure 5.6c).

Ammonium concentrations where highest between the 4th of July and 24th of July 2012, with levels below the thermocline (mean 3 m), ranging between 0.12 mg N L^{-1} to 0.52 mg N L^{-1} (Figure 5.6b). As concentrations of NH_4-N in the hypolimnion increased during this stratified period (4th of July to the 24th of July 2012), DO concentrations decreased, for instance the highest level of NH_4-N concentration (0.52 mg N L^{-1}) occurred at 9 m on the 24th of July which coincided with the lowest DO concentration (2.52 mg L^{-1}) recorded at the 7 m DO sensor. From the 1st of August to the 17th of September 2012, NH_4-N levels were homogenous throughout the water column, with a mean value of 0.14 mg N L^{-1} (Figure 5.6b).

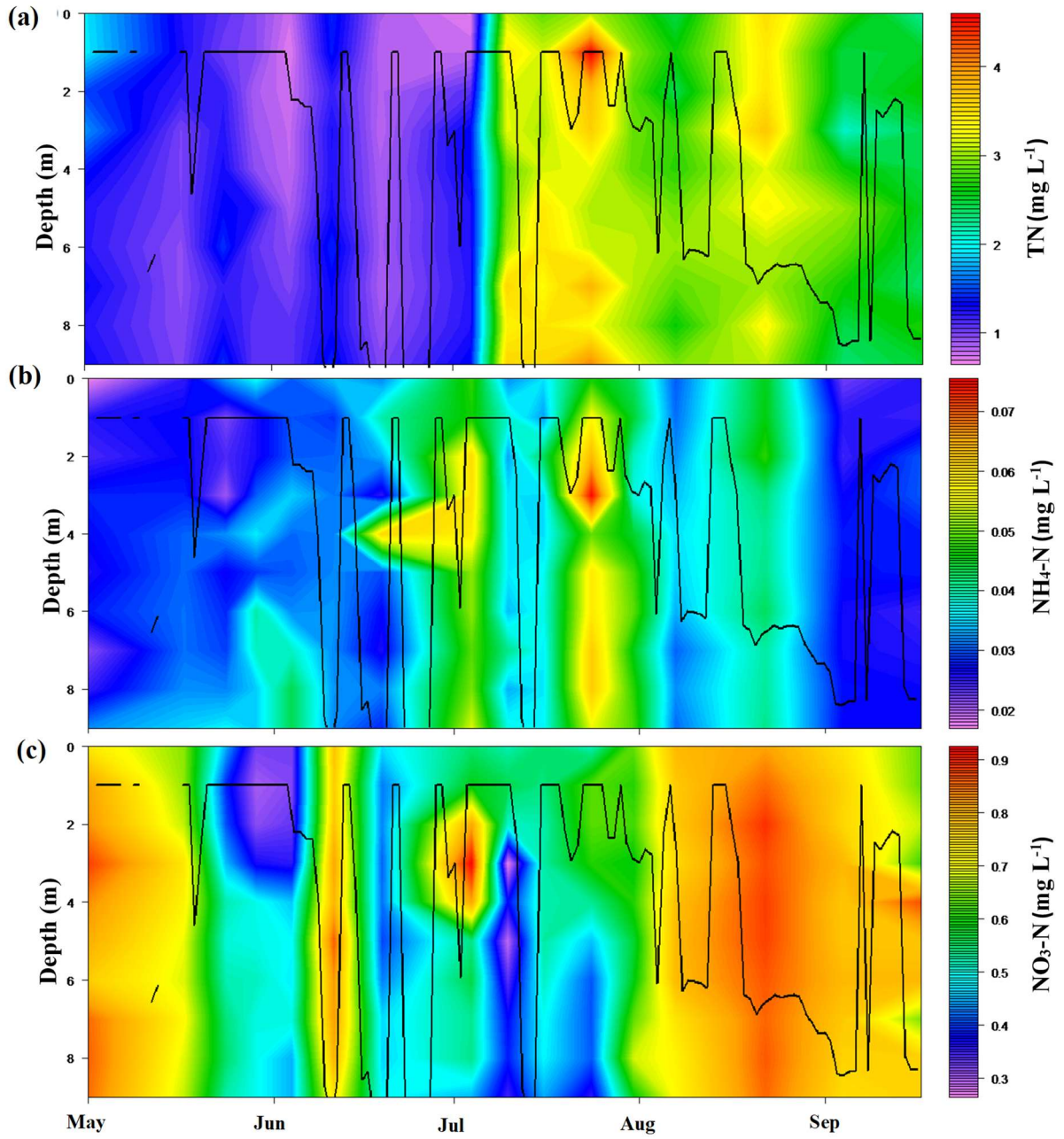

Figure 5.6 Contour plots of **(a)** TN (mg L^{-1}), **(b)** ammonium (NH_4-N) (mg L^{-1}) and **(c)** nitrate (NO_3-N) (mg L^{-1}), with thermocline depth at the deepest point in Milltown Lake, superimposed (m), between the 1st of May 2012 and the 17th of September 2012.

5.5.4 Drivers of chlorophyll a concentration (1st of May to the 17th of September 2012)

For all depths, physical and meteorological variables were the main drivers of change in Chl-*a* concentrations, rather than in-lake nutrient concentrations or inflow nutrient loads (Table 5.2). Two disturbance factors, wind speed ($p = 0.0067$) and stream discharge ($p = 0.0100$), explained 53% of the deviance in Chl-*a* concentrations at the lake surface (0.1 m) (Table 5.2). The relationships were generally positive and linear (estimated degrees of freedom (edf)) of 1.5 and

1.1 for wind speed and stream discharge, respectively (Figure 5.7a, b). At the 2 m depth interval, S was the dominant driver ($p = 0.0008$), with wind speed still significant but having a weaker relationship ($p = 0.0358$). This model explained a higher portion of the deviance, however, with a R^2 adjusted of 0.74 (Table 5.2). The relationship to stability was curvilinear with Chl-*a* biomass peaking at a stability of 20 J m^{-2} to 30 J m^{-2} and decreasing at higher levels (Figure 5.7c). At all of the remaining three depth intervals, and in contrast to the two shallower sampling levels, mean thermocline depth and PAR were significant terms in the optimum model. In addition, it is of note that the only nutrient term that was significant in any of the models, NH_4-N, explained a portion of the deviance at two of the lower sampling depths (4 m and 6 m). The optimum models explained 90%, 84%, and 73% of the deviance at 4 m, 6 m, and 8 m, respectively (Table 5.2). The relationship between biomass and mean thermocline depth was generally negative, that is Chl-*a* concentrations were higher as the thermocline depth became shallower. This term was most significant at 4 m but less significant as depth increased (Table 5.2). In contrast the relationship between Chl-*a* concentrations and estimated PAR levels was generally positive (Figure 5.7f, i, l), with the exception of the 4 m depth where higher Chl-*a* levels coincided with both low and high PAR levels. At both the 6 m and 8 m depths, PAR was a more significant term in the optimum model than mean thermocline depth ($p = <0.0001$, $p = 0.0003$ respectively) (Table 5.2). Lake NH_4-N concentrations were significant at both 4 m and 6 m only (Table 5.2) with higher Chl-*a* levels coinciding with both high and low NH_4-N concentrations at the 4 m depth (Figure 5.7g), and a weak but negative relationship indicated at 6 m (Figure 5.7j).

Table 5.2 GAM model for the drivers of Chl-*a* concentrations (µg L^{-1}) at the surface, 2 m, 4 m, 6 m and 8 m depth intervals at the deepest point in Milltown Lake.

Level	n	Parameter	Edf	p	R^2 adjusted
Surface	14	Wind speed	1.50	0.0067	0.53
		Stream discharge	1.10	0.0100	
2 m	14	S	1.97	0.0008	0.74
		Wind speed	1.91	0.0358	
4 m	14	Mean thermocline depth	1.96	0.0023	0.90
		PAR	1.99	0.0005	
		Lake NH_4	1.98	0.0008	
6 m	14	Mean thermocline depth	1.00	0.0146	0.84
		PAR	1.96	<0.0001	
		Lake NH_4	1.00	0.0351	
8 m	14	Mean thermocline depth	1.00	0.0465	0.73
		PAR	1.93	0.0003	

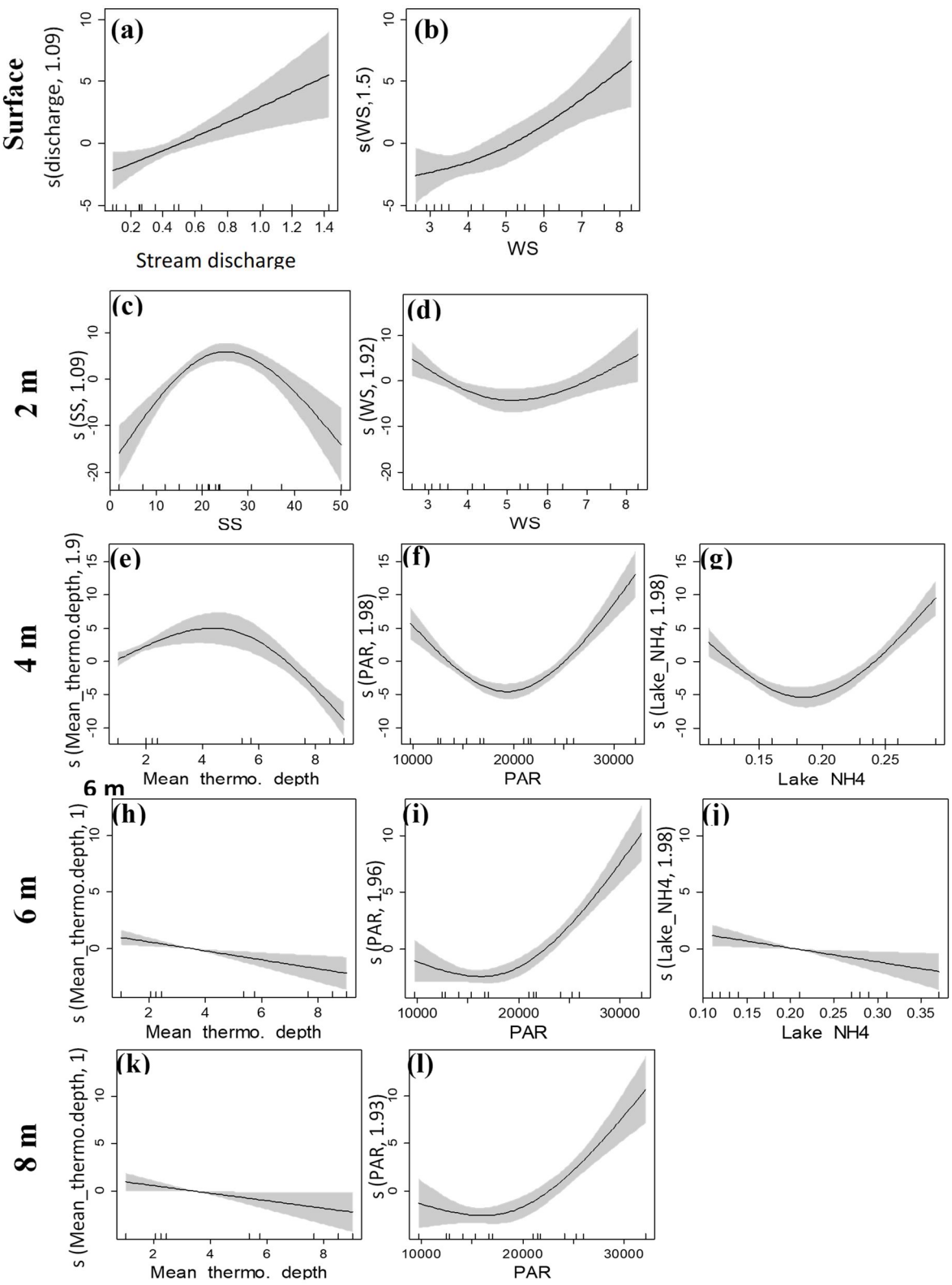

Figure 5.7 Estimated smoothing curve for chlorophyll *a* concentrations (μg L^{-1}) at the surface **(a)** stream discharge, **(b)** WS (wind speed); 2 m **(c)** S (Schmidt stability), **(d)** WS (wind speed); 4 m **(e)** mean thermocline depth, **(f)** PAR (photosynthetically active radiation), **(g)** Lake NH_4; 6 m **(h)** mean thermocline depth, **(i)**, PAR (photosynthetically active radiation) **(j)** Lake NH_4 and at the 8 m **(k)** mean thermocline depth, **(l)** PAR (photosynthetically active radiation) intervals at the deepest point in Milltown Lake. Grey shaded area indicates the 95% confidence bands.

5.6 Discussion

Local weather conditions govern many of the physical aspects of lake ecosystems, which are important drivers of change in phytoplankton assemblage (Reynolds, 2002; Blenchner et al., 2007). The high resolution temperature measurements from Milltown Lake indicated that the lake, at times, fluctuated between mixing and stratifying during the summer seasons. This thermal regime is indicative of the thermal behaviour of a small polymictic lake (Hutchinson, 1957; Woolway et al., 2017). The polymictic nature of Milltown Lake was previously noted by Carson et al. (2015). However, that study was based on weekly temperature profiles taken over the summer months in 2007-2008. Ireland has an oceanic climate that is relatively mild, with high levels of precipitation and highly variable wind speeds (Keane, 1986). The comparison of climatic and in-lake thermal conditions for Milltown Lake indicated that, in 2010, the air temperature range was greater during the study period months (1st May to the 17th of Sept 2010), than in the following two years. The wind speed range and the stream discharge within the catchment was also lower in 2010. It is important to note that both 2010 and 2011 had a greater number of drier low flow periods than the study year, 2012. In response to these conditions, the lake stratified for longer periods in 2010 and there was a stronger S, buoyancy frequency and Wn and a more consistent and stable thermocline depth. In contrast the opposite weather conditions were seen in 2011 and 2012, resulting in weaker periods of stratification and thermocline stability. The main factors that contributed to this in 2011 and 2012 were wind speed and air temperature, while in 2012 additional pressures, including periods of higher rainfall and, as a result, greater daily stream discharge also played a significant role. The transient stratifications that were seen in Milltown Lake are commonly seen in polymictic lakes, for example, Lough Neagh (Northern Ireland), Bassenthwaite Lake (UK) or Rotorua (New Zealand), where wind and convective mixing are the most common driving factors (Woolway et al., 2014).

In addition to climatic effects on the lake thermal structure caused by changes in wind speed and rainfall, high rainfall also results in day to day changes in nutrient loading to lakes, particularly in agricultural catchments (Jordan et al., 2005; Macintosh et al., 2011). Analysis of nutrient losses from 17 catchments covering different climatic conditions across Europe, carried out by Bouraoui et al. (2009), found that climatic variables, in particular total rainfall, explained most of the variation in the nutrient load at the catchment's outlet (Nõges et al., 2011). This effect of high rainfall on loading was particularly evident for Milltown Lake in 2012. Nutrient availability and grazing pressures are generally considered to be the main controls on phytoplankton biomass in lakes (Teissier et al., 2011). Generally, temperate lakes experience nutrient limitation due to reduced inflow and higher uptake rates at some point during the growing season, especially when the lake is stratified (Wetzel, 2001), although, seasonal anoxic conditions can result in nutrient release from the sediments to the hypolimnion (O'Dwyer et al., 2013).

It was particularly notable that nutrient levels in the study lake remained high throughout the wet summer of 2012. Such conditions are not uncommon in the oceanic temperate climate of western Europe and, indeed, may become more common in more regions in response to directional climate change (Paerl et al., 2016). The availability of daily nutrient loading data, together with high frequency temperature and nutrient data along a depth profile provided a unique opportunity to assess the relative importance of both physical conditions and nutrients as drivers of phytoplankton biomass in the surface water and at depth. Studies of the drivers of phytoplankton biomass over a lake's entire depth profile are rare (Brentrup et al., 2016).

The GAM analysis indicated that both nutrient and climatic drivers affected Milltown Lake's phytoplankton differently along the lake depth profile. The percentage deviance explained at all depths was high, ranging from 53% to 90%, giving confidence in the model output.

However, it is of note that the main driving variables that were identified differed for the surface and deeper layers, and that climate-related factors dominated at all depths. In the surface waters of Milltown Lake, mean daily wind speed and stream discharge showed significant positive relationships with Chl-*a* levels suggesting that disturbance and surface mixing were the factors controlling phytoplankton standing stock, as measured by Chl-*a.* Moreno-Ostos et al. (2009) reported that chlorophyll fluorescence in the upper and surface layers of a small lake responded rapidly to wind stresses. They suggested that wind-induced mixing enabled internal nutrient mixing, facilitated phytoplankton species to remain in suspension, allowed species replacement and transported species from deeper waters to the upper water column. Wu et al. (2010) measuring Chl-*a* as a proxy for phytoplankton standing stock, reported that wind conditions affected phytoplankton distribution through advective water movements over a short time frame in Lake Taihu, China. The consistent high levels of discharge to Milltown Lake after the beginning of June 2012 would also have contributed to mixing in the surface waters. It was notable that neither TP nor TN loading to the lake were significant terms in the optimum model for the surface layer, but that inflow discharge was. This confirmed that the effect was related to the physical effects of inflowing water rather than to any nutrient effect. The strong influence of stream discharge as a physical driver in Milltown Lake was particularly evident on the 8th of June 2012, when the initial early summer period of strong stratification was broken down by a high stream discharge event (4.25 m^3 sec^{-1}). Wind speed at this time did not increase and was relatively low at 3.0 m^3 sec^{-1}. Along with this de-stratification, a high pulse of both TP and TN was carried into the lake from the catchment during this event.

The 2 m sampling depth was beneath the shallow thermocline in May, but at or above the mean thermocline depth in July and August. Schmidt stability is the stability of a waterbody and its resistance to mixing, therefore the amount of work required to transform a waterbody to a uniform water density state (Wetzel, 2001). Schmidt stability was a significant term in the GAM

model at the 2m depth in Milltown Lake, with highest Chl-*a* concentrations occurring at intermediate stability levels of around 30 J m^{-2}. This indicated that, at this depth, as the lake became more stable and less prone to wind mixing stresses, phytoplankton biomass increased. This may have resulted the formation of a cyanobacteria bloom in the epilimnion of Milltown Lake, as lake stability due to decreased wind stresses is important factor in the formation of cyanobacteria blooms in the upper epilimnion (Ibelings et al., 1994; Huisman et al., 2004; Monero-Osten et al., 2009).

Both physical factors (mean thermocline depth and PAR) and one nutrient factor (NH_4 concentration within the lake) were drivers of phytoplankton biomass in the deeper waters, below 4 m. Solar radiation levels, on which PAR was based, were obtained from a meteorological weather station 52 km south-west of Milltown Lake. However, the existence of this relationship suggests that they adequately captured conditions at the lake. The mean photic zone depth (Luhtala and Tolvanen, 2013) (2.5 times mean Secchi depth) of 3.6 m in this eutrophic lake was greater than the mean thermocline depth (2.8 m) on 7 of the 15 sampling occasions between 1st of May 2012 and the 1st of October 2012. Simmonds et al. (2015) found, for a highly eutrophic lake in New Zealand (Lake Ōkaro), that the photic zone was greater than the thermocline depth and the Chl-*a* maximum for the duration of their study. Simmonds et al. (2015) described this pattern as being typical for the Chl-*a* maximum formation in clear water lakes where the photic zone always exceeds the depth of the lower metalimnion. However, this pattern is not commonly seen in many eutrophic lakes systems.

The depth of the photic zone in Milltown Lake, below the thermocline depth, may explain why PAR was a significant driver of phytoplankton biomass in the hypolimnion. Chlorophyll *a* can become concentrated at discrete depths where there may be contrasting gradients in light and nutrients that limit light availability (Simmonds et al., 2015). It is likely therefore, that

phytoplankton in the hypolimnion of Milltown Lake could survive below the thermocline depth due to receiving adequate PAR levels. Some species can also migrate to ensure optimum PAR levels. Diatoms, for example, can have reduced settling rates at the thermocline (Coon et al., 1987), and cyanobacteria can regulate buoyancy (Padisa'k et al., 2004; Carraro et al., 2012), while ciliates and dinoflagellates are motile (Modenutti et al., 2004; Simmonds et al., 2015). Even though no underwater PAR measurements were available, the significance of PAR in the GAM models, and indeed the fact that the maximum Chl-*a* was recorded at lower depths in the lake on 7 of the 15 sampling occasions, indicate that PAR was reaching the lower waters below the thermocline. The relationship of Chl-*a* to thermocline depth was negative, that is higher phytoplankton biomass occurred when the overlying epilimnion was shallow. Since phytoplankton only have a short generation time, they show a quick response to changes in their environmental conditions (Lebret et al., 2012). Therefore, a shallow thermocline would allow phytoplankton in the lower hypolimnion of Milltown Lake to be circulated toward upper layers and increased light exposure.

The export of nutrients from catchments to lakes is strongly influenced by land use practices (Vanni et al., 2010). Milltown Lake is situated in an agricultural catchment with high rainfall and a flashy hydrology (Carson et al., 2015). The estimated annual loads from the Milltown Catchment, measured in the present study at the lake inlet were 0.58 kg TP ha^{-1} yr^{-1} and 8.03 kg TN ha^{-1} yr^{-1}, respectively. In an Irish context, loads to Milltown Lake from the catchment were at the mid to high range of the scale compared to losses presented by Jordan et al. (2012) from two intensive grassland catchments (0.17 - 0.78 kg TP ha^{-1} yr^{-1} and 8.9 - 28.8 kg TN ha^{-1} yr^{-1}), and Jordan et al. (2005) from three grassland catchments (0.17 to 3.13 kg TP ha^{-1} yr^{-1}). These loads would have included those from the fenced western tributary, where mitigation measures have already been implemented and have been shown to potentially decrease export during summer (Chapter 4). Catchment farming activities, such as organic and inorganic

fertiliser spreading during spring and summer months, would have contributed to the observed high nutrient loading to the lake, maintaining the lake in a high nutrient state.

As reported by Carson et al. (2015) for Milltown Lake and similar to the last two decades, the lake was eutrophic in summer 2012 based on the O.E.C.D classification scheme (Taylor et al., 2002). However, although lake TP and TN concentrations were consistently high throughout the water column during the current study, NH_4-N levels were found to be a significant driver of Chl-*a* levels in the lower waters. Ammonium is preferred by phytoplankton due to it being readily assimilated into cells compared to NO_3-N which must be transformed by nitrate reductase before it can be metabolised (Reynolds, 1997; Burger et al., 2008; Simmonds et al., 2015). The observed relationship to NH_4-N suggests that the phytoplankton species within the hypolimnion were N limited. Additionally, this study has shown that internal loading can be involved in the control of phytoplankton biomass in a shallow eutrophic lake which is already under stress from external nutrient loading.

Management of excessive phytoplankton production is usually achieved through a reduction in P inputs from the catchment, as P is often regarded as the limiting nutrient (Carpenter et al., 1998; May et al., 2009). Moss et al. (2013) suggested that this is often the case due to a long held presumption that restricting N load in freshwaters is pointless, due to N control being more complex and expensive than P control particularly from diffuse sources (Directive 91/676/EEC). Nonetheless, our results clearly showed that N can be a limiting factor for phytoplankton biomass, as NH_4 concentrations accumulated from decomposing organic matter and sediment release can stimulate phytoplankton growth, exhibit toxicity to aquatic biota, and exert an oxygen demand on the surface waters (Directive 91/676/EEC; Wetzel, 2001; Beutel, 2006). Therefore, management strategies for this catchment need to consider for both P and N control. On-going and projected climate change can have a profound effect on nutrient loading

in catchments that have a flashy hydrology by delivering high nutrient loading, particularly before the onset of stratification (Crockford et al., 2015; Jeppesen et al., 2010, 2011; Moss et al., 2011). As Milltown Lake is an agricultural catchment that is prone to high rainfall, nutrient inputs from this source are a primary concern particularly when considering lake restoration approaches. Results show that, not only is Milltown Lake impacted by surface nutrient loading, but sediment nutrient release, particularly NH_4, may also be a contributing factor. Management strategies are mainly devised to target nutrient loads from the surrounding catchment. However, more attention is needed in understanding the internal lake sediment release, as it is considered to play a significant role in the years after catchment loading have been reduced (Jeppesen et al., 2010). Management strategies in more recent years are looking at using geo-engineering materials (lanthanum modified bentonite and aluminium) for controlling P release from bed sediments, particularly in shallow eutrophic lakes (Copetti et al., 2016). The main premises behind this is that, by controlling internal P loading the ecological effects of eutrophication can be rapidly reversed (Mackay et al., 2014; Copetti et al., 2016). However, the chemical behaviour and effectiveness of these materials varies and, therefore, more comprehensive research needs to be carried out before being rolled out as a viable remedial management measure for these eutrophic lake systems (Spears et al., 2013).

5.7 Conclusion

This study has provided new insights into why depth and time related differences occur in phytoplankton biomass in small lakes. In particular, it highlighted the role that climatic factors play in influencing phytoplankton biomass throughout the whole lake profile, directly at the surface, and where the photic zone reaches below the thermocline depth. These insights are important on a global scale, not only because small water bodies such as Milltown Lake (surface area 0.14 km^2, average depth of 5.5 m) are far more common world-wide than the iconic, charismatic lakes often studied (e.g. Lake Constance; surface area 563 km^2, average depth of 90 m) (Downing et al., 2006; Verpoorter et al., 2014), but because of on-going changes in local

weather patterns. In addition, this study highlighted how discrete surface sampling, which is a common protocol for many lake nutrient monitoring programmes, may not provide an overall picture of the complex processes occurring throughout the lake's depth profile.

Chapter 6: Influences of multiple drivers on phytoplankton diversity in Milltown Lake during spring stratification

6.1 Abstract

Determining how phytoplankton species or group abundance is influenced by the balance between changes in water column stability, and other factors such as nutrient availability and zooplankton grazing, during the onset of spring stratification is an important element in understanding lake ecosystems. This is particularly so for Milltown Lake given the significant impacts of physical and meteorological drivers of Chl-*a* identified in Chapter 5. This chapter builds on those findings, focusing especially on the spring and early summer period in Milltown Lake, when the lake structure generally changes rapidly from fully mixed to a stratified state. Data were obtained on the physical characteristics of the lake temperature profile, nutrient concentrations at 1 m intervals, and on the plankton communities, over an intense 10 week sampling period carried out in 2013. Results from the GAM analysis for Milltown Lake, indicated that light and P availability were more influential at the upper epilimnion, while N availability was more influential in controlling the standing stock of phytoplankton at the lower depths. Diatoms (*Asterionella* sp. and *Cyclotella* sp.) were identified as the dominate taxa, during the spring bloom formation at both Depth 1 (sub-surface) and Depth 2 (the extent of the photic zone) in Milltown Lake, which conforms with seasonal patterns outlined in the Plankton Ecology Group (PEG) model. Data from the principal component analysis (PCA) showed little influence of zooplankton grazing at either depth. Overall, these findings have outlined how complex a lake's community structure is and that many different factors, both climatic and nutrient related, play a role in its overall status.

6.2 Introduction

6.2.1 Phytoplankton

Phytoplankton are considered to be the dominant producers of energy in lakes and represent the largest source of biomass in a freshwater ecosystem. The growth of phytoplankton and presence

varies seasonally and results from the supply of nutrients and light availability within a lake (Xu et al., 2010; Cunha Pereira et al., 2011; Edwards et al., 2016; de Eyto et al., 2016). In addition, certain phytoplankton groups have the ability to adjust their migration behaviour, shape, size or through adaptation to physical factors such as water movements within a lake. This helps them to remain in the upper photic zone, therefore, improving the interception of light (Coon et al., 1987; Padisa´k et al., 2004; Modenutti et al., 2004; Reynolds, 2006; Carraro et al., 2012; Simmonds et al., 2015). Examples include the Cyanobacteria, a phylum of bacteria that, due to their photosynthetic capabilities, are included among the algal collections. Cyanobacteria remain buoyant in the upper water column by using their gas vacuoles as floatation devices while *Cryptophyta, Pyrrhophyta* and *Chrysophyta* stay mobile using flagella. Phytoplankton can also adapt to maximise light absorbance, through adjusting their pigment concentration level by altering their feeding strategies (Proctor and Roesler, 2010). Once these demands are satisfied, phytoplankton can experience rapid growth, leading to large biomass accumulation in the upper layers referred to as phytoplankton bloom (Martinez et al., 2011).

Phytoplankton spring blooms are a global phenomenon in temperate aquatic ecosystems, and the timing and magnitude of the spring bloom prompts much of the subsequent dynamics in a lake ecosystem throughout the year (Platt et al., 2003; Edwards and Richardson, 2004). As a result, a major focus for plankton ecologists has been to explain the mechanisms driving the onset of the phytoplankton spring bloom and its dynamics (Riley, 1942; Sverdrup, 1953; Atkins, 2009; Lewandowska et al., 2015). The role of light availability and water column mixing processes in bloom formation have been emphasised by researchers since the 1920s (Gran and Braarud, 1935; Lewandowska et al., 2015). In the early 1940s, the compensation depth concept was introduced by Riley (1942). This is the depth at which photosynthesis exactly matches respiration rate. In 1950s, Sverdrup (1953), incorporated all of these concepts and proposed the first quantitative explanation of the occurrence of the spring phytoplankton bloom. Since then,

there have been several advances in explaining spring bloom formation. These highlight the role of turbulence, grazing by zooplankton and nutrient concentrations in controlling phytoplankton blooms (Fischer *et al.*, 2014). However, the critical depth hypothesis (Sverdrup, 1953) remains the most widely cited (Lewandowska et al., 2015). In general terms, the spring phytoplankton bloom occurs as a result of the upper water column having sufficient availability of nutrients brought to the surface by deep winter mixing, or by inflows from the catchment, coupled with higher levels of irradiance, all of which combine to give ideal conditions to support rapid phytoplankton growth (Martinez et al., 2011). The magnitude and duration of the spring phytoplankton bloom are mainly controlled by a variety of factors including water temperature, stratification of the water column, availability of light and nutrients, and losses due to zooplankton grazing and respiration (Lucas et al., 1999; Peeters et al., 2007; Behrenfeld 2010; Schabhüttl et al., 2013).

Phytoplankton community structure has been the subject of intense study for many decades (Riley, 1942; Sverdrup, 1953; Atkins, 2009; Deng et al., 2014). The spring bloom is now recognised to consist of a series of sequential blooms involving different phytoplankton species (Lewandowska et al., 2015). Shifts in the dominant phytoplankton species are likely caused by biological and physical factors. For instance, increased nutrient loads are considered to be one of the main drivers of cyanobacterial dominance and blooms in lakes. However, Deng et al. (2014), also suggests that cyanobacteria dominance can shift to chlorophytes under excessive nutrient loading, as chlorophytes in temperate lakes are characterised by high growth and loss rates, and high nutrient demands, while cyanobacteria often have lower growth and loss rates due to their ability to convert inert atmospheric nitrogen into an organic form such as NO_3 and NH_3, thus lowering their demand for nutrients. Furthermore, climate change maybe an additional pressure on the qualitative change in phytoplankton community dynamics. Climate can impact phytoplankton both directly through physiology and indirectly by changing water

column stratification and resource availability, mainly nutrients and light, or intense grazing by heterotrophs (Jeppesen et al., 2009; Jeppesen et al., 2011; Winder and Sommer, 2012). Such modifications affect various phytoplankton processes, and a widespread advance in phytoplankton spring bloom timing and changing bloom magnitudes have both been observed (Brookes and Carey, 2011; Jeppesen et al., 2011). Such shifts in phytoplankton composition can have a far reaching consequence for ecosystem structure and functioning, and thus an improved understanding of the mechanistic links between climate and phytoplankton dynamics is important for predicting climate change impacts on aquatic ecosystems (Winder and Sommer, 2012).

Dominant phytoplankton groups within relatively shallow lake ecosystems include fast-growing unicellular nanoplanktic forms (e.g. *Chlorella*, *Monoraphidium* spp.), nanoplanktic flagellates (*Chlamydomonas, Plagioselmis, Chrysochromulina*), chrysophycean (especially *Synura* spp.) and small volvocalean colonies (especially *Gonium*) (Reynolds, 2006). Within Ireland, Free et al. (2006) in a study of 201 lakes located across the isle of Ireland, identified Desmids, Merismopedia dinoflagellates (Pyrrophyta), Gymnodinium, Ceratium, diatoms (Bacillariophyta), *Peridinium* spp. and *Dinobryon* spp. to be the most common phytoplankton groups.

6.2.2 Zooplankton

Patterns in zooplankton seasonal succession are mainly influenced by the availability of food and temperature, with an increase in zooplankton assimilation of algae and bacteria occurring at higher temperatures (Wetzel, 2001). There are two dominant groups of zooplankton found in freshwater lakes, cladocerans (e.g. *Diaphanosoma brachyurum*, *Bosmina* sp., *Ceriodaphinia* sp. and *Daphnia* sp.) and copepods (e.g. *Calanoida* spp., *Cyclopoida* spp. and juvenile calanoids or cyclopoids known as nauplii). Zooplankton exhibit diel vertical migration, which refers to

the migration of zooplankton to deeper waters during the day and to the surface at night (Williamson et al., 2011; Armengol et al., 2012). Williamson et al. (2011) proposed that this behaviour was a response to biotic factors such as food and predation, and abiotic factors such as light and temperature. Wetzel (2001) described migration behaviour at night as a means of going unnoticed by predators such as fish, and also of allowing zooplankton to take full advantage of the high phytoplankton biomass in the upper waters.

Zooplankton have the ability to influence the seasonal succession of phytoplankton and significantly impact the overall productivity of a lake's ecosystem (Jeppesen et al., 2000; Sommer et al., 2012). Different zooplankton species exhibit diverse behaviours for acquiring their food. Some species of zooplankton as selective feeders, grazing on detrital material and autochthonous phytoplankton. Cyclopoids are predatory and are regarded as selective feeders, feeding mainly on rotifers, flagellates, ciliates and nauplii (Faithfull et al., 2011; May and Wallace, 2019). Calanoids are omnivorous filter feeders and are selective as they asses the nutritional quality of their prey or plankton population (McCarthy et al., 2006). *Daphnia*, in contrast, are known as non-selective feeders and utilise a wide range of particles, grazing on phytoplankton and organic detritus including bacteria (Carney and Elser, 1990; Perga and Gerdeaux, 2006).

6.2.3 Deep Chlorophyll Maximum (DCM)

The vertical distribution of chlorophyll in stratified lakes frequently displays a peak deep in the water column, which is referred to as the deep chlorophyll maximum (DCM) (Simmonds et al., 2015; Leach et al., 2018). The zones where this occurs are ecologically important hotspots for nutrient cycling and primary production, and their position can determine the vertical habitat gradient for phytoplankton (Leach et al., 2018). Deep chlorophyll maxima are commonly found in optically deep, low productivity lakes, and less so in eutrophic systems (Serizawa et al., 2010;

Simmonds et al., 2015). In a study by Hamilton et al. (2010), they suggest that a DCM in a lake formed only when the euphotic zone exceeded the maximum depth of the epilimnion. Several studies have also reported this close relationship, including those by Heaney and Talling (1980), Whittington et al. (2000) and Modenutti et al. (2004). Further drivers for the formation of a DCM in a lake include the vertical distribution of nutrients and the location of the thermal gradients in the water column (e.g. Fee, 1976; Abbott et al., 1984; Cullen, 2015; Leach et al., 2018). It is the thermal stratification layer that determines the depth of the DCM, as it can regulate nutrient mixing from deep waters into the euphotic zone (Abbott et al., 1984; Varela et al., 1994; Mellard et al., 2011; White and Matsumoto, 2012). Additionally, it is believed that the metalimnion offers protection from surface driven mixing that could entrain phytoplankton into the upper mixed layer and exposed populations to potentially harmful levels of irradiance (Abbott et al., 1984; Kamykowski and Yamazaki, 1997; Whittington et al., 2000; Simmonds et al., 2015). Taxa commonly found in the DCM can vary in their behaviour and physical adaptations and may include groups such as the diatoms which have reduced settling rates at the thermocline, buoyancy regulating cyanobacteria, and motile ciliates and dinoflagellates (Coon et al., 1987; Modenutti et al., 2004; Padisa'k et al., 2004; Carraro et al., 2012; Simmonds et al., 2015).

6.2.4 PEG model concept

The Plankton Ecology Group is a conceptual model to explain the seasonal patterns of change in phytoplankton biomass (Sommer et al., 1986; Sommer et al., 2012; De Senerpont Domis et al., 2013). The PEG model uses 24 sequential steps to discuss the abiotic and physical mechanisms and biotic interactions with zooplankton that occur during the spring growing season (Sommer et al., 1986), and remains one of the most cited models in plankton ecology (Carey et al., 2016). According to the PEG model, in eutrophic system, it is expected that the community would exhibit two or three distinct peaks within a year: a spring bloom of diatoms,

a summer bloom of chlorophytes and/or cyanobacteria, and potentially an autumn diatom bloom (Sommer et al., 1986, Sommer et al., 2012). Possible triggers for phytoplankton spring blooms in freshwater lakes, as outlined by Reynolds (2006), are the temperature and light regime within the lake ecosystem. However, in an updated PEG model, Sommer et al. (2012), assessed these possible triggers of the phytoplankton spring bloom and concluded that, although temperature played a vital role, light was the dominant factor that triggered blooms in spring. Various deviations from the PEG models have been documented over the past number of years in several lakes (Jeppesen et al., 1997; Alvarez-Cobelas et al., 2005; Moustaka-Gouni et al., 2014), mainly relating to advances in the understanding of the microbial loop, phytoplankton food quality for example. However, the PEG template provided an important starting point for examining lake phytoplankton community dynamics (Free et al., 2006; Pociecha et al., 2010; Padisa'k et al., 2010; Carey et al., 2016).

Milltown Lake was one of eleven lakes in the GLEON Spring Blitz, a project established in 2012 to determine how phytoplankton richness is influenced by changes in water column stability during the onset of spring stratification. The work described in this chapter contributed to that project, but also was expanded to fulfil specific aims for the studies undertaken at Milltown Lake and to build on the work described in Chapter 5. The aims of Spring Blitz were based on the concepts of the PEG model. Sampling was undertaken at the deepest point in the lake to examine the role that water column stability (over space and time) played in determining plankton diversity. Sampling of physical parameters, nutrient concentrations and plankton communities were conducted (~ every 3-4 days) during the spring period of 2013. In addition to that protocol, further nutrient and Chl-*a* sampling was undertaken at 1 m depth intervals in a way that was similar to the sampling protocol seen in Chapter 5 in Milltown Lake, to allow comparison with data from the previous study year (2012).

6.3 Aims of this study

The primary aim of the research presented in this chapter was to study the role that the balance between changes in water column stability, nutrient availability, and zooplankton grazing played in determining plankton diversity in the study lake at the surface and at the photic depth. The latter depth was chosen to represent the extent of the euphotic zone. The study was focused on the spring and early summer period when the lake structure went from fully mixed to a stratified state over a very short time period.

6.4 Methods

Monitoring of Milltown Lake took place in the weeks prior to and during the on-set of stratification, in spring 2013. High resolution data for DO concentrations and % saturation, and temperature were obtained from *in-situ* lake sensors (described in Section 3.5). Analytical methods for nutrients and Chl-*a* analyse for monitoring at the lake inflow and at the deepest point within the lake are described in Sections 3.4 and 3.6 (Figure 3.1b).

6.4.1 Sampling depth calculation and abiotic sampling protocol

Milltown Lake was sampled bi-weekly (each Tuesday and Thursday), at the deepest point in the lake (~10 m), for a period of 10 weeks (18th of April 2013 to the 20th of June 2013). This period included the weeks leading up to and the 5 weeks after the initial onset of thermal stratification (Figure 3.1b). The depth at the deepest point on the day of sample collection was measured using a handheld Hondex (PS-7) Portable Depth Sounder. The approximate timeframe of the onset of thermal stratification was based on the stratification patterns of Milltown Lake in previous years (Figure 5.3a). The onset of the lake thermocline (defined as a one degree centigrade change in temperature per metre) was monitored using a chain of nine TidbiT temperature loggers, recording temperature at 15 minute intervals (Section 3.5).

Two sampling depths were measured: Depth 1 (0.1 m below the lake surface) and Depth 2 (Secchi depth measurement, Figure 6.1) (Luhtala and Tolvanen, 2013). Depth 2 was sampled as being the extent of the euphotic zone and to investigate the occurrence of any potential DCM (Simmonds et al., 2015). The Secchi depth was measured using a 20 cm diameter Secchi disk. The disk was lowered on the shady side of the boat and the depth at which the disk disappeared was recorded to the nearest 0.1 m. The disk was then slowly hauled up and the depth at which the disk reappeared was again recorded to the nearest 0.1 m. The Secchi disk transparency was calculated according to the following equation:

$$\text{Secchi depth} = (d_1+d_2) / 2 \qquad \text{(Equation 6.1)}$$

Where d_1 is the depth (m) at which the disk disappeared and d_2 is the depth (m) at which the disk reappeared; 2 is the number of measurements recorded.

Based on the Secchi depth sampling, the depths determined were calculated as follows:

Depth 1: Subsurface sample (0.1 m below lakes surface) (Figure 6.1).

Depth 2: Secchi depth measurement recorded on sampling day (potential for DCM) (Figure 6.1).

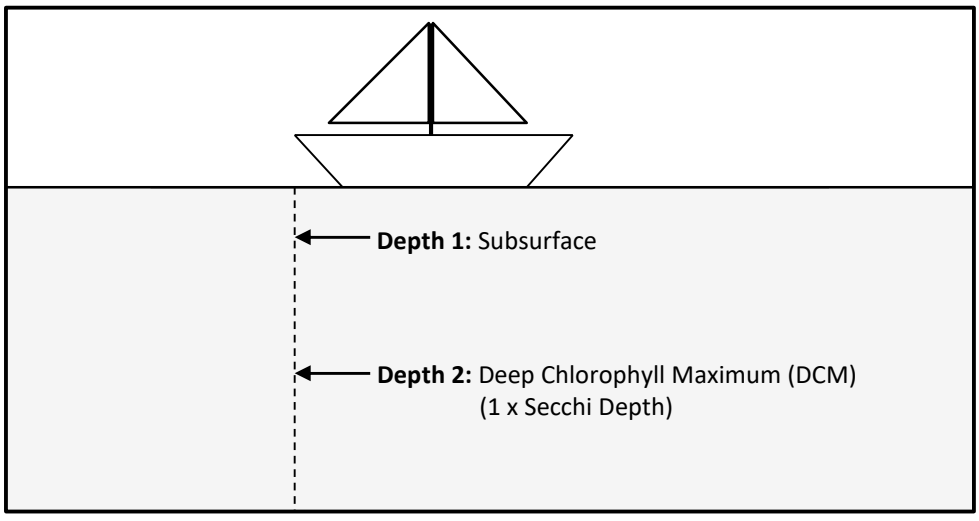

Figure 6.1 Sampling depths in Milltown Lake in spring 2013.

Additional measurements on each sampling occasion included water column DO (mg L^{-1} and % SAT) using a YSI 556 MPS multi probe with a 30 m extension, to verify the *in-situ* sensor data. The portable YSI multi probe was calibrated in the laboratory prior to carrying out field work and assessed periodically throughout the sampling trip.

Water samples were collected at the deepest point within Milltown Lake, at sampling Depths 1 and 2, and addition at 1 m intervals (1, 2, 3, 4, 5, 6, 7, 8 and 9 m) throughout the lake profile for comparison purposes with the sampling protocol used in 2012 (Chapter 5). Samples were collected using a Fieldmaster® Basic Van Dorn sampler and analysed for nutrients, total P, total N, SRP, NH_4-N and NO_3-N (Figure 3.1b). Samples for Chl-*a* were also collected using the Fieldmaster® Basic Van Dorn sampler at 0.1, 2, 4, 6 and 8 m, in the same sampling location to allow comparison with the previous sampling year (Chapter 5). Water samples (nutrient and Chl-*a*) were collected using pre-acid washed 2 L polyethylene bottles, rinsed with ultrapure water. Sample bottles were rinsed with lake water from the depth to be sampled prior to sample collection. Methods used for the analysis of total nutrients, dissolved nutrients and Chl-*a* are described in Section 3.4 and 3.6.

Daily composite samples for determining TP and TN load were collected using a HACH® Sigma 900 Max autosampler during the study period. The autosampler was located at the EPA staff gauge on the Drumleek River, 500 m upstream from the only lake inflow (Figure 3.1a). The sampler was programmed to collect six 50 ml samples per day at 4 hour intervals, giving a final daily sample volume of 300 ml. The polyethylene sample bottles were pre-acid washed and rinsed with Milli-Q water. Sample bottles were collected on the same days as the lake samples. Stream discharge data from an EPA managed staff gauge provided stream discharge data at 15 minute intervals.

6.4.2 Collection of biotic parameters based on Secchi depth measurements

Phytoplankton and zooplankton samples were collected from Depth 1 and Depth 2 only using a Fieldmaster® Basic Van Dorn sampler. Phytoplankton samples were preserved by adding 2-3 ml of Lugol's iodine to a 200 ml glass amber bottle, the bottles were capped and shaken until well mixed. Zooplankton samples were narcotised by adding 2 Alka-seltzer® tablets, which narcotises the organisms, to a 250 ml wide necked plastic bottle, to which 99% industrial methylated spirits were added for preservation. All sample bottles were rinsed with lake water from the depth being sampled prior to sample collection.

6.4.3 Phytoplankton counting

Counting of preserved phytoplankton was based on the sedimentation technique developed by Utermohl in 1958, the standard method used in WFD (EN 15204 2006) (European Standards, 2006). The phytoplankton samples were mixed gently by rotating the sample bottle in a figure of eight motion for 20 revolutions to thoroughly mix the contents. A 25 ml Utermohl sedimentation chamber was filled with a pipette to the top with sufficient excess to create a bead of water. A glass cover was then placed on top of the sedimentation chamber to remove the excess water and to enclose the exact column of sample without entrapping water bubbles. Algae were allowed to settle to the bottom of the sedimentation chamber. To ensure complete sedimentation of the sample, the sedimentation time should be twice the volume of the sedimentation chamber (25 ml) (Margalef, 1969), therefore, each sample was allowed to settle for approximately 48 hours prior to counting. Identification and enumeration of phytoplankton samples was conducted under an inverted microscope (Leica™ S 80/0.30) at a defined magnification. The microscope was linked to a camera that enabled accurate phytoplankton measurements to be calculated from the images. Measurements were taken from images calibrated using a 1 mm stage micrometre. At low magnification (x 100), an individual overview of the content of the chamber was carried out, with records made of any large individual organisms and unusual specimens in the sample which may not appear at subsequent

finer examination. Empty cells were not counted. Three randomly chosen transects of the chamber were counted (x 400) to identify and enumerate the organisms present.

Samples were identified to genus and species level, where possible, by using taxonomic references (Huber-Pestalozzi, 1983; Whitton and Brook, 2003; Berllinger and Sigee, 2010). As far as possible, filamentous or colony formations were counted as individual colonies. Phytoplankton abundance (numbers L^{-1}) and biomass (pg C ml^{-1}) were calculated for Depth 1 and Depth 2.

6.4.4 Zooplankton counting

Zooplankton sample containers were inverted a number of times to ensure a mixed sample was being analysed. Samples were initially filtered through a 64 µm filter and washed with deionised water to remove the alcohol preserve. The sample was then transferred into a graduated cylinder and diluted to 50 ml with deionised water. From this two 5 ml sub-samples were subsequently transferred using a wide bored 5 ml pipette to a Ward rotary chamber. The samples were measured and counted under an Olympus SZX12 stereoscope microscope at a magnification of x 25. Two sub-samples were enumerated from the two sampling depths (Depth 1 and Depth 2) on all sampling dates. Zooplankton individuals were identified to groups (Cladocerans and Copepods) and to genus level (*Daphnia* sp., *Ceriodaphnia* sp., *Diphanosoma* sp. and *Bosmina* sp.), calanoids and cyclopoids, using the Harding and Smith (1974), Pontin (1978) and Scourfield and Harding (1994) identification keys. The first 50 individuals encountered were measured in length and width. Zooplankton abundance (numbers L^{-1}) was calculated based on estimating the number of individuals per litre, while biomass (pg C ml^{-1}) was calculated based on the length-weight relationship (Bottrell et al., 1975; McCauley, 1984; Pauli, 1989).

6.4.5 Other data

Flow and meteorological data (Ballyhaise and Coose Met Éireann weather stations) were available for the 10 week sampling period (Figure 3.1; Figure 3.4). Photosynthetically Active Radiation measurements were estimated from hourly SW radiation from the Ballyhaise Met Éireann weather station. The SW (Wm^{-2}) was subsequently converted to PAR ($\mu E\ m^{-1}\ sec^{-2}$) by multiplying the SW radiation by 0.45 (Pinker et al., 2010). Daily nutrient loads of the catchment area were calculated for the inflow site as the product of concentration and expressed in $g\ ha^{-1}\ day^{-1}$. Schmidt stability and thermocline depth were determined from vertical temperature profiles using the LakeAnalyzer programme (Read et al., 2011) (Section 3.7). Thermocline depth calculations excluded the uppermost 0.5 m of the water column due to diurnal surface water heating sometimes creating a strong but temporary (diurnal) density gradient (Simmonds et al., 2015).

6.4.6 Data analysis

Statistical analyses were carried out using the R statistical package version 3.2.2 (R 195 Core Team, 2015) and Microsoft Excel (2013). General additive modelling was used to identify the main drivers of estimated Chl-*a* concentrations. Analysis was carried out using the mgcv package (Wood, 2006) in R (version 3.2.5, R 195 Core Team, 2015). The spreads of the residuals were relatively homogenous, indicating that a Gaussian distribution was appropriate for the model (Zuur et al., 2009). All data sets were assessed for any breaches of the assumptions of independence and heteroscedasticity using the methods in Zuur et al. (2009). All data sets conformed to these assumptions. Principal Component Analysis was used to assess the change in phytoplankton species abundance prior to and after the onset of spring thermal stratification. Analysis was carried out using the vegan package (Wood, 2006) in R (version 3.2.5, R 195 Core Team, 2015). Various data sets were used during the analysis (catchment nutrient loading, internal lake nutrient loading, meteorological data and zooplankton taxa) to separate the effects of individual drivers on phytoplankton species response.

6.5 Results

6.5.1 Meteorological and in-lake vertical temperature profile data

The mean daily air temperature during the study period (18th of April to the 20th June 2013) was 10.6 ºC, with a maximum air temperature of 15.3 ºC recorded on the final day of the study. The average precipitation was 2.2 mm day^{-1}, with the maximum daily precipitation (13.2 mm day^{-1}) coinciding with a peak in stream discharge on the Drumleek River, occurring the day prior to the lake becoming thermally stratified on the 26th of May 2013 (Figure 6.2a). The average daily wind speed for the study period was 3.4 m sec^{-1}.

A period of higher PAR levels was recorded in late May, with a maximum of 663 µE m^{-1} sec^{-2} on the 30th of May. The photic depth of Milltown Lake on this date was 5.5 m (Figure 6.2c). Stratification of Milltown Lake occurred during this period of high PAR, and the lake then

remained stratified until the end of the 10 week sampling period. The photic depth of Milltown Lake during this stratified period ranged between 4.4 m and 7.4 m (2.5 x Secchi depth measurement), which was relatively similar to the depth range (3.5 m to 7.5 m) of the photic zone prior stratification. The thermocline depth during stratification ranged from 1 m and then progressively increased to a maximum depth of 3.7 m on the 17th of June 2013. The surface mixed layer temperatures during stratification were relatively low and ranged from 13.1 ^{o}C (26th of May 2013) to 19.7 ^{o}C (10th of June 2013), while the air temperature during the stratified period ranged between 10.0 ^{o}C (31st of May 2013) and 15.3 ^{o}C (20th of June 2013) (Figure 6.2d).

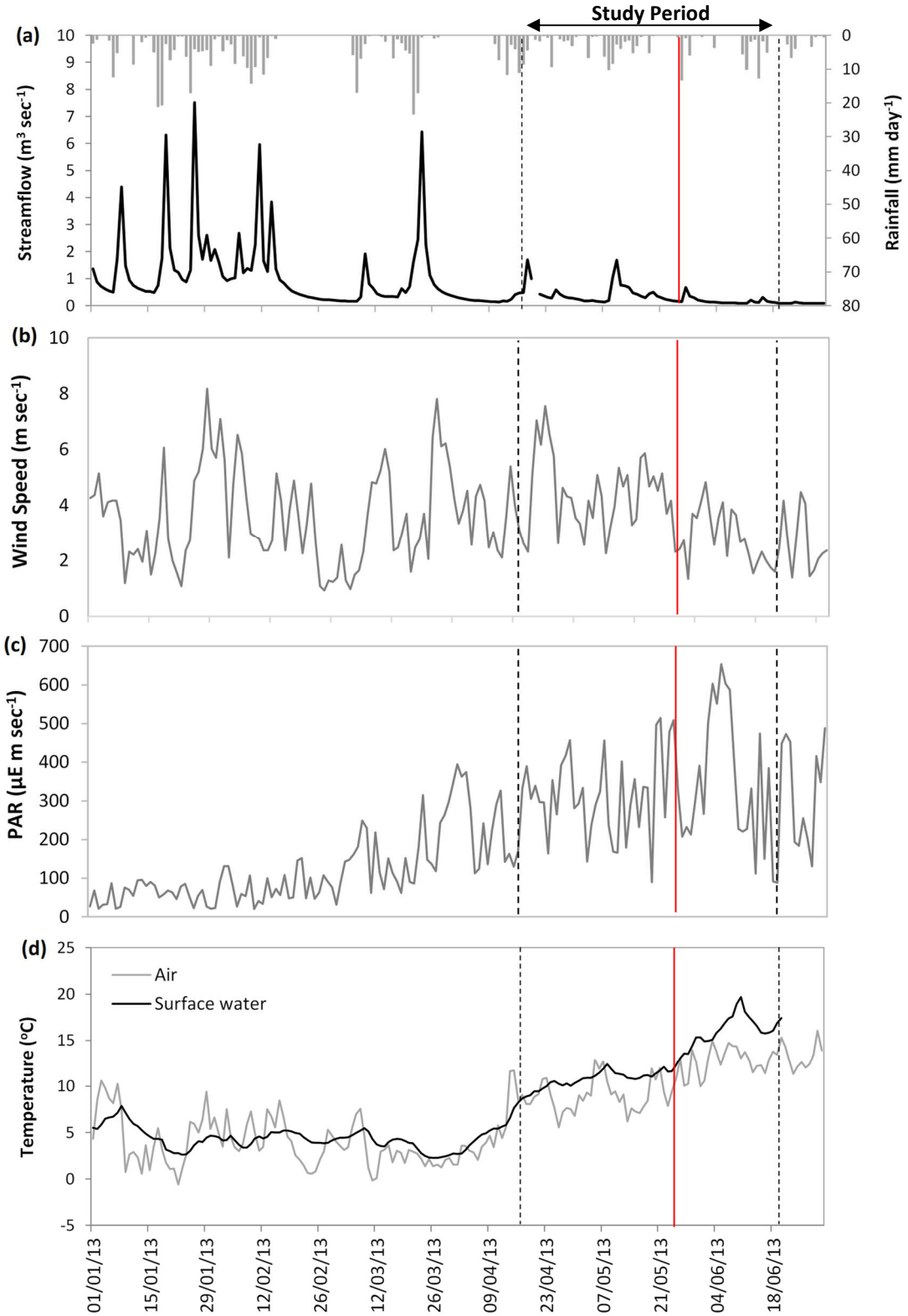

Figure 6.2 (a) daily rainfall (mm day^{-1}) at Coose Met Éireann weather station and stream discharge (m^3 sec^{-1}) for the EPA staff gauge site on the Drumleek River, **(b)** daily average wind speed for Milltown Lake, **(c)** daily average photosynthetically active radiation (PAR) from the Ballyhaise Met Éireann weather station and **(d)** daily average surface water temperature for Milltown Lake and air temperature from the Ballyhaise Met Éireann weather station, for six month period (January to June 2013). The area between the dashed lines indicates the study period. The red line indicates the day on which the lake stratified (26th May 2013).

Average daily TP and TN loads entering Milltown Lake over the study period from the catchment were 3.2 g P ha^{-1} d^{-1} and 44.3 g N ha^{-1} d^{-1} respectively. The two weeks prior to stratification (26th May) had the highest nutrient loads from the catchment, with peak loads coinciding with increases in stream discharge (20.6 g TP ha^{-1} d^{-1} and 163.0 g N ha^{-1} d^{-1}) (Figure 6.3a). The mean DO concentration recorded during the 10 week study was 11.0 mg L^{-1} at 1 m, and 7.9 mg L^{-1} at 7 m. Prior to the onset of stratification (26th of May 2013), DO concentration ranged between 10.0 mg L^{-1} and 13.8 mg L^{-1} at the 1 m depth and between 9.1 mg L^{-1} and 12.0 mg L^{-1} at 7 m. However, DO concentration declined at the 7 m depth following stratification to a low of 0.4 mg L^{-1} on the 20th of June 2013 (Figure 6.3b). Milltown Lake became fully stratified on the 26th of May 2013, when the depth of the thermocline was 1.0 m, the stratified layer deepened to a depth of 2.8 m and remained stratified until the end of this study (Figure 6.3c). During this stratified period, the mean water temperature for the surface mixed layer was 14.3 ^{o}C, while the mean water temperature beneath the thermocline depth was 11.0 ^{o}C. Schmidt stability increased gradually during this stratified period (mean of 28.6 J m^{-2}) with a three day period of higher values occurring in early June (57.8 J m^{-2} on the 8th of June to 46.6 J m^{-2} on the 10th of June 2013) (Figure 6.3d). This coincided with the maximum surface water temperature of 21.4 ^{o}C on the 9th of June 2013 (Figure 6.3c).

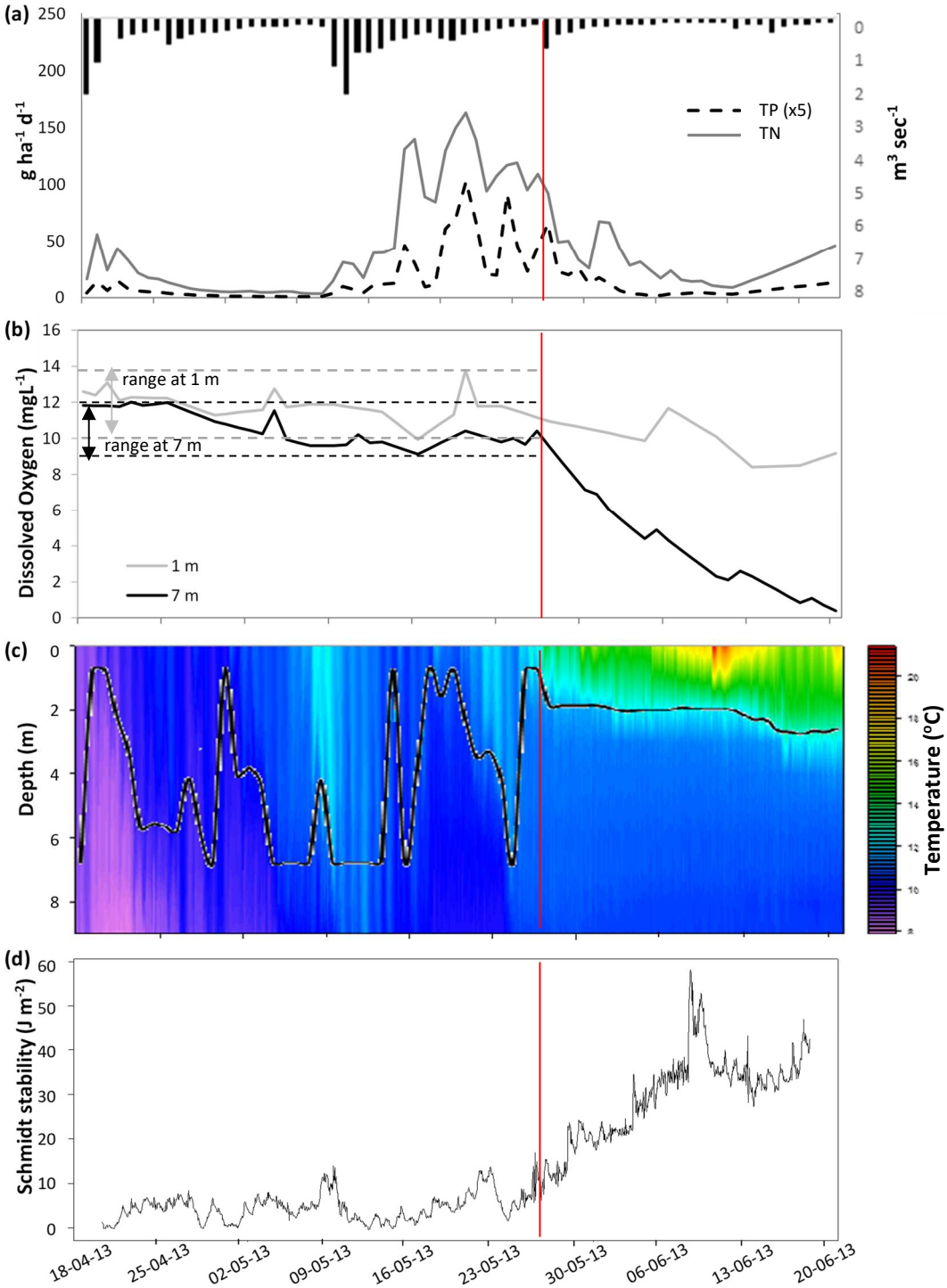

Figure 6.3 (a) stream discharge (m^3 sec^{-1}) and nutrient loadings (g ha^{-1} d^{-1}) from the lake inlet site, **(b)** dissolved oxygen (mg L^{-1}) at 1 m and 7 m depth. The grey area between the grey dashed line indicates the range for DO at 1 m and the area between the black dashed line indicates the range for DO at 7 m. **(c)** contour plot of lake temperature (°C) with thermocline depth (m) superimposed and **(d)** Schmidt stability (J m^{-2}), between the 18 April 2013 and the 20 June 2013. Note difference in scale for TN and TP loads, where TP concentrations are multiplied by a factor of 5. The red line indicates the start of thermal stratification in Milltown Lake.

6.5.2 Lake abiotic data

Phosphorus concentrations in the lake ranged between 0.009 – 0.179 mg TP L^{-1} for TP and between 0.009 – 0.065 mg SRP L^{-1} for SRP. High concentrations of TP (mean 0.082 mg P L^{-1}

throughout the water column) were recorded three days prior to the lake stratifying (26th of May 2013), between the 16th of May 2013 and the 23rd of May 2013, coinciding with the pulse in nutrient loading into the lake, but also with high Chl-*a* levels (Figure 6.4a, b). Total P concentrations then decreased following stratification, however, there was a peak in TP levels on the 13th of June 2013, with maximum concentrations (0.179 mg P L^{-1}) above the photic zone (bottom of photic zone depth measuring 6.7 m) (Figure 6.4b). Increased SRP concentrations (averaged at 0.030 mg P L^{-1}) were seen throughout the water column at the start of the study period (18th of April 2013). Higher concentrations of SRP were evident in the photic zone for the remainder of the study period (> 0.030 mg L^{-1}), indicating nutrient input from the Milltown Catchment, while below the photic zone SRP concentrations were below 0.010 mg L^{-1}, indicating SRP was not being released from the lake sediment. (Figure 6.4c). The mean SRP concentration in the photic zone was 0.031 mg SRP L^{-1}, while mean concentration below the photic zone was 0.008 mg SRP L^{-1}.

During the first three weeks of the sampling campaign, the mean TN concentrations were less than 1.2 mg N L^{-1} for all depths. However, similar to TP, concentrations increased throughout the water column prior to stratification (26th of May 2013), with maximum levels reaching 2.1 mg TN L^{-1} (≤ 1m) on the 16th of May 2013 (Figure 6.4d). During stratification, the mean TN concentration was 1.4 mg TN L^{-1}, with higher concentrations in the lower water depths after the 6th June 2013 (Figure 6.4d). High NO_3-N concentrations were found throughout the water column during the first two weeks of the study period, with concentrations ranging between 0.5 mg NO_3-N L^{-1} to 1.2 mg NO_3-N L^{-1} (Figure 6.4e). However, during the stratified period, higher NO_3-N concentrations were generally observed below the photic zone ranging between 0.18 mg NO_3-N L^{-1} to 0.71 mg NO_3-N L^{-1}. Following stratification, when the DO concentration at the 7 m depth declined (becoming fully anoxic on the 20th of June 2013), NH_4-N concentrations were higher at the lower depths (range: 0.08 NH_4-N L^{-1} – 0.61 NH_4-N L^{-1}), possibly indicating

release of NH_4-N from the sediment. Ammonium concentrations peaked in the deeper waters on the 30th of May ranging between 0.24 mg NH_4-N L^{-1} to 0.51 mg NH_4-N L^{-1} and remained high until the end of the sampling period (Figure 6.4f).

Between the 16th of May 2013 and the 23rd of May 2013, just before stratification but following the high loadings of nutrients to the lake, high Chl-*a* concentrations were recorded throughout the water column, with the maximum Chl-*a* of 62 µg L^{-1} recorded on the 23rd of May 2013 at the surface (Figure 6.4a). However, at the onset of stratification 26th May 2013, Chl-*a* concentrations at the surface sampling depth (0.1 m) reduced to 21.7 µg L^{-1}. During the stratified period, there was a further peak in Chl-*a* concentration (65 µg L^{-1}) at the surface sampling depth (0.10 m) on the 10th of June 2013. This peak in Chl-*a* concentration at the surface depth reduced to 25 µg L^{-1} by the end of the sampling campaign (20th of June 2013) (Figure 6.4a). Chlorophyll *a* at the lower depths were generally lower than those recorded at the surface depths (range: 4 µg L^{-1} – 29 µg L^{-1}). However, on the 13th of June there was a peak in Chl-*a* recorded at 2.7 m (42 µg L^{-1}), the Chl-*a* at the surface depth on this date measured 23 µg L^{-1}.

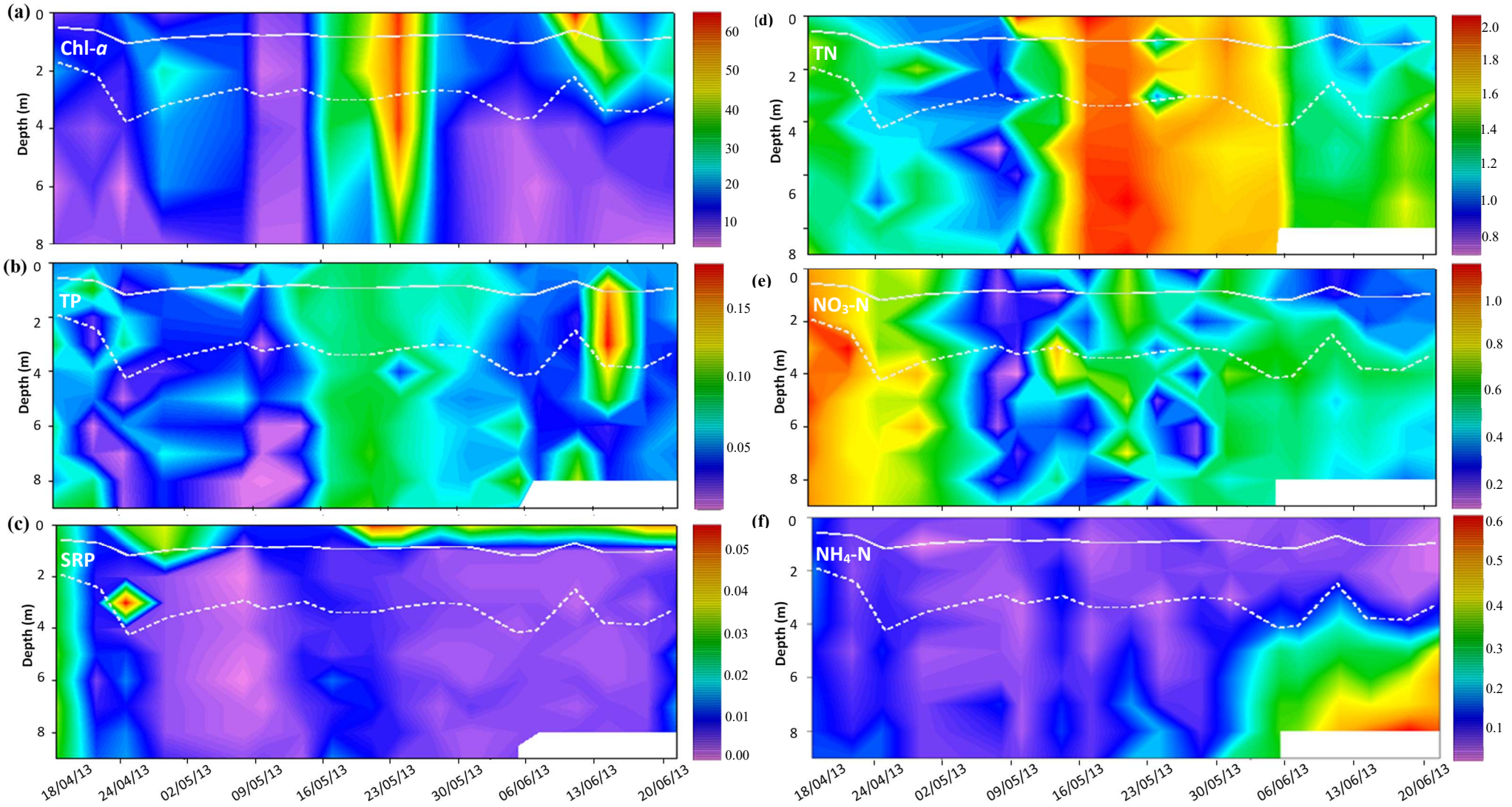

Figure 6.4 Contour plots of **(a)** chlorophyll *a*, **(b)** total P, **(c)** soluble reactive phosphorus, **(d)** total N, **(e)** nitrate (NO_3-N) and **(f)** ammonium (NH_4-N) concentrations with Secchi depth indicated by the solid white line and the bottom of the photic zone indicated by the dashed white line superimposed (m), at the deepest point in Milltown Lake, between the 18 April 2013 and the 20 June 2013. All units are in mg L^{-1}, with the exception of Chl-*a* which is in µg L^{-1}. The white section at the lower righthand corner of the figure denotes a lowering in lake water level.

6.5.3 Drivers of chlorophyll a concentration

Interestingly, for all depths, nutrient variables were the dominant drivers of change in Chl-*a* concentrations (Table 6.1). At the surface sampling depth, PAR levels (PAR_3D ($p = 0.0002$), lake TP concentrations (Lake_TP) ($p = 0.0106$) and Lake_SRP ($p = 0.0465$)) explained 74% of the deviance in Chl-*a* concentrations (Table 6.1). This GAM for the surface water depth explained the highest % deviance of the models for all depths. The relationships were all positive (edfs of 1.96, 1.90 and 1.00 for PAR_3D, Lake_TP and Lake_SRP respectively) (Table 6.1; Figure 6.5a, b, c). At the 2 m depth interval, a weak relationship with the TN loading from the catchment (TN_catch_load) was identified ($p = 0.0319$), however, this explained only 32% of the deviance (Table 6.1). This weaker relationship for TN was also evident at the next lowest 4 m depth interval ($p = 0.0269$, R^2 adj = 0.27) (Table 6.1). At the two lower depths (6 m and 8 m) the optimum models indicated that in-lake nitrogen again played an important role in plankton biomass (Figure 6.5d, e). Both Lake_TN ($p = 0.0009$) and Lake_NH_4 ($p = 0.0147$) showed a positive relationship with Chl-*a* concentrations (Table 6.1; Figure 6.5f, g). A strong positive relationship (edf of 1.9) between Chl-*a* concentration and Lake_TN only was also observed at 8 m ($p = <0.0001$), explaining 67% of the deviance in Chl-*a* at this depth (Figure 6.5h).

Table 6.1 GAM model for the drivers of chlorophyll *a* concentration (µg L^{-1}) at the surface, 2 m, 4 m, 6 m and 8 m depth intervals at the deepest point in Milltown Lake.

Level	n	parameter	edf	P	R^2 adj
Surface	18	PAR_3D Lake_TP Lake_SRP	1.96 1.90 1.00	0.0002 0.0106 0.0465	0.74
2 m	18	TN_catch_load	1.68	0.0319	0.32
4 m	18	TN_catch_load	1.32	0.0269	0.27
6 m	18	Lake_TN Lake_NH4	1.00 1.89	0.0009 0.0147	0.56
8 m	18	Lake_TN	1.94	<0.0001	0.67

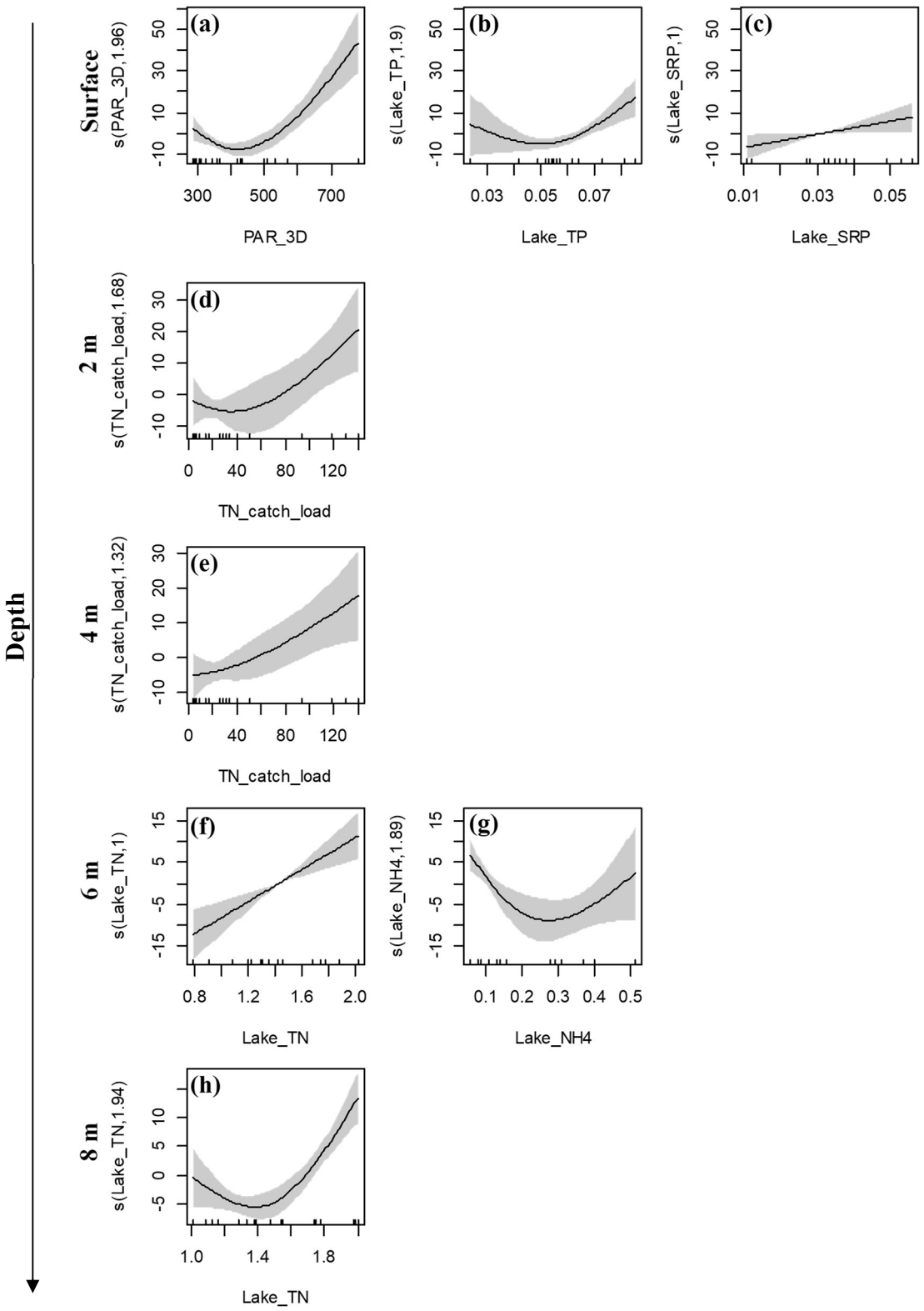

Figure 6.5 Estimated smoothing curve for chlorophyll *a* concentration (μg L^{-1}) at the surface **(a)** PAR_3D, **(b)** Lake_TP, (**c**) Lake_SRP, 2 m **(d)** TN_catch_load, 4 m **(e)** TN_catch_load, 6 m **(f)** Lake_TN, **(g)**, Lake_NH4 and 8 m **(h)** Lake_TN, depth intervals at the deepest point in Milltown Lake. Grey shaded area indicates the 95% confidence intervals. PAR = photosynthetically active radiation.

6.5.4 Lake biotic data: phytoplankton species composition and abundance

During the initial weeks of the sampling campaign, prior to the onset of thermal stratification in Milltown Lake, peaks in both the Chlorophytes (dominated by the species *Stichococcus sp* and *Mougeotia sp)* and Euglenophytes (*Euglena* spp. and *Trachelomonas volvocina* groups were observed at Depth 1 (0.1 m below the surface) (Figure 6.6a). Chlorophytes contributed 40% to 80% of the total numbers of cells counted during this time (Figure 6.7a). This dominance shifted to the Cyanophytes just prior to the onset of thermal stratification (which then represented between 50% to 70%). These were dominated by *Zygenema* species (Figure 6.6a, Figure 6.7a). The Cryptophyte plankton group (*Cryptomonas sp* and *Rhodomonas sp*) then began to increase at Depth 1, peaking on the 27th of May, the day after stratification occurred in the lake. This group remained dominant until the 10th of June 2013, contributing between 70% to 90% (Figure 6.6a, Figure 6.7a).

At Depth 2 (Secchi depth) in the weeks prior to stratification in Milltown Lake, the Chlorophytes were the main plankton group, contributing between 40% to 55%. These were dominated by *Mougeotia* species (Figure 6.6b, Figure 6.7b). There was a shift in group dominance once the lake stratified on the 26th of May, with the Crytophytes (*Cryptomonas sp* and *Rhodomonas sp*) peaking on the 30th of May 2013 and the Bacillophytes (*Astrionella sp*) peaking shortly after on the 04th of June 2013 (Figure 6.6b). However, toward the end of the sampling period the Chlorophytes once again dominated Milltown Lake at Depth 2, contributing between 50% to 60% of the total phytoplankton population, with the dominant species changing from *Mougeotia sp* (evident prior to stratification) to *Stichococcus sp* (Figure 6.6b, Figure 6.7b).

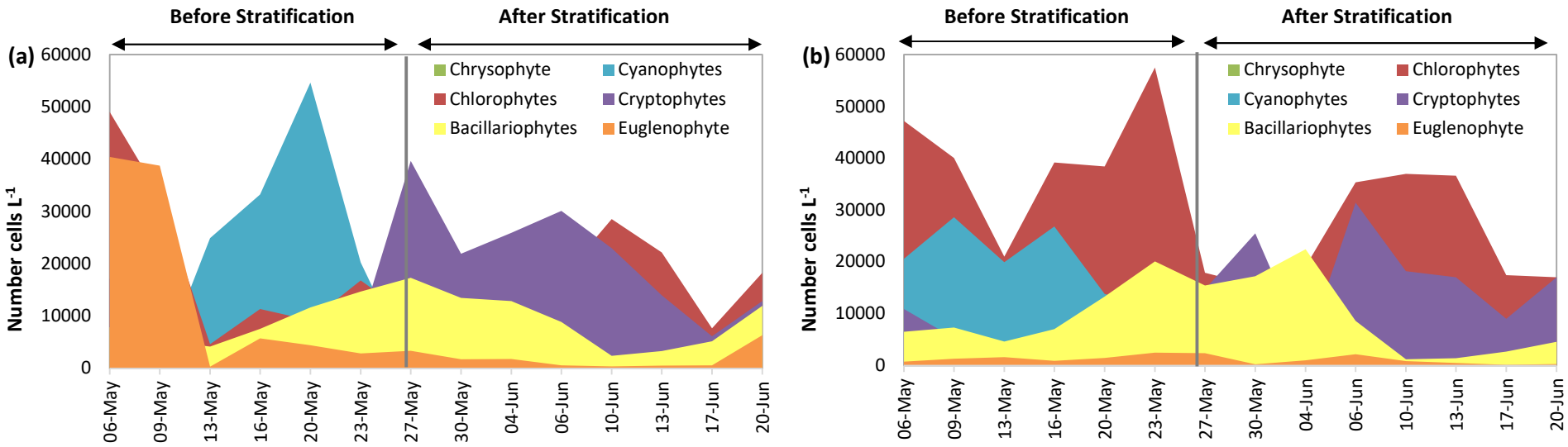

Figure 6.6 (a) Phytoplankton abundance (Number L^{-1}) counted at Depth 1 (0.1 m below the surface) and **(b)** Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake.

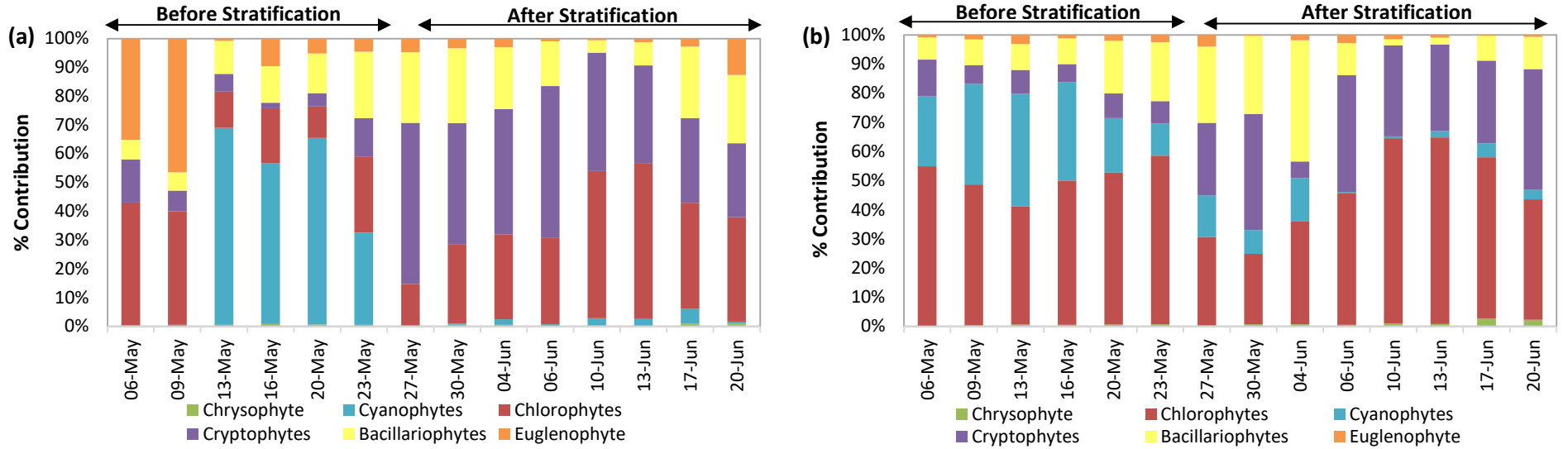

Figure 6.7 (a) Percentage contribution (based on abundance) of Phytoplankton enumerated at Depth 1 (0.1 m below the surface) and **(b)** Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake.

6.5.5 Phytoplankton biomass

In general. in the weeks prior to stratification, the phytoplankton biomass for the different groups at both Depth 1 and Depth 2 in Milltown Lake were considerably lower than on the days after stratification occurred (Figure 6.8a, b). At Depth 1 Cyanophytes (*Zygenema* spp.) biomass peaked on the 13th of May at 27 pg C ml^{-1} and remained high until the 16th of May (22.9 pg C ml^{-1}) (Figure 6.8a). Even though the Bacillophytes (*Astrionella sp* and *Cyclotella sp*) were not the most numerous species in the days prior to and during the onset of stratification, they had the largest biomass during this period, and steadily increased and peaked at 21.8 pg C ml^{-1} on the 30th of May 2013 (Figure 6.8a). However, once stratification was established in Milltown Lake, Cryptophyte (*Cryptomonas sp* and *Rhodomonas sp)* biomass dominated, peaking at 59.6 pg C ml^{-1} on the 06th of June 2013 (Figure 6.8a.).

The Raphidophytes (*Gonyostomum sp*) had the largest biomass in the days immediately prior to stratification at Depth 2 (9th May to the 20th of May 2013) peaking at 30.5 pg C ml^{-1} on the 16th of May (Figure 6.8b). This then shifted to the Bacillophytes (*Astrionella sp*) which increased in biomass prior to and during the onset of thermal stratification in Milltown Lake peaking at 60.9 pg C ml^{-1} on the 04th of June 2013 (Figure 6.8b).

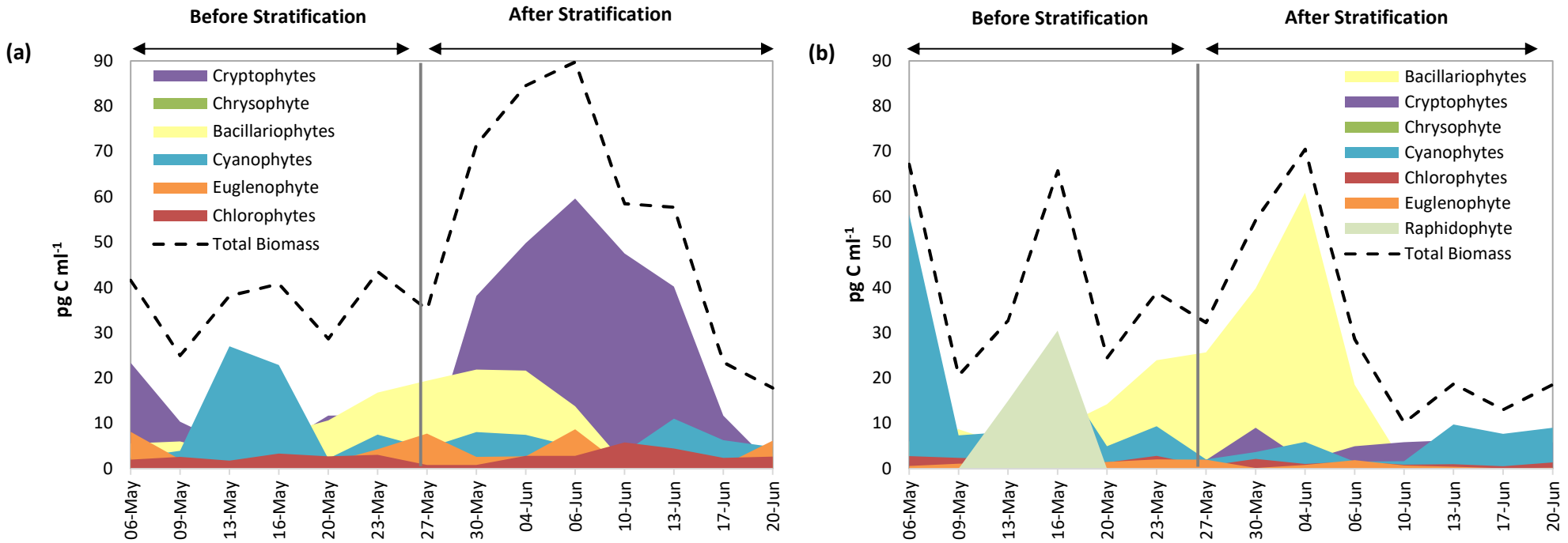

Figure 6.8 (a) Phytoplankton biomass (pg C ml^{-1}) counted at Depth 1 (0.1 m below the surface) and **(b)** Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake

6.5.6 Zooplankton species composition and abundance in terms of population densities.

The three main zooplankton taxa that dominated Milltown Lake in the days prior to stratification at Depth 1 were *Keratella* (20% to 30% contribution by population density), *Ascomorpha* (40% contribution) and *Asplancha* (70% to 85% contribution) (Figure 6.9a, Figure 6.10a). However, once Milltown Lake stratified on the 26th of May 2013, the taxal dominance shifted to *Brachionus* (65% to 75% contribution by population density), which peaked on the 30th of May (Figure 6.10a). This dominance was short lived as the main zooplankton taxa dominance after the onset of stratification was *Keratella* (95% contribution by population density) (Figure 6.9a, Figure 6.10a). Overall, at Depth 2, there was a higher number of zooplankton individuals across all sampling dates (Figure 6.9b). *Keratella* was generally the dominant zooplankton taxa throughout the sampling campaign. *Ascomorpha* (contributing 45%) were but for a short period in the days prior to stratification, peaking on the 13th of May (Figure 6.9b, Figure 6.10b). As seen in Depth 1, the *Brachionus* assemblage increased post-stratification peaking on the 4th of June (Figure 6.9a, b). This was shortly followed by *Conochilus* which peaked on the 10th of June (Figure 6.9b).

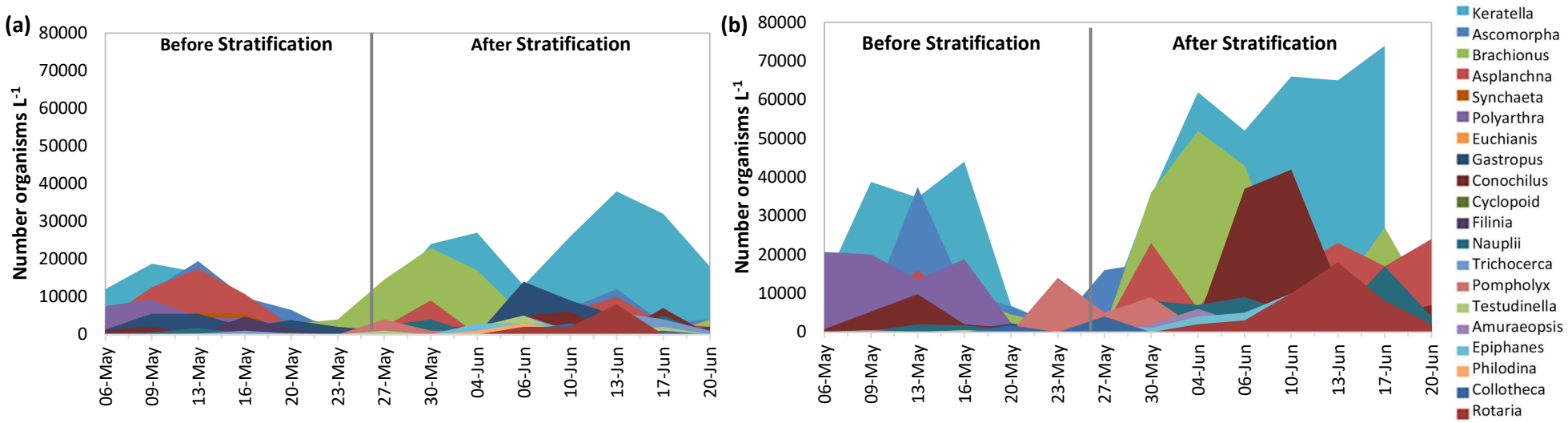

Figure 6.9 (a) Zooplankton abundance (Number L^{-1}) counted at Depth 1 (10 cm below the surface) and **(b)** Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake.

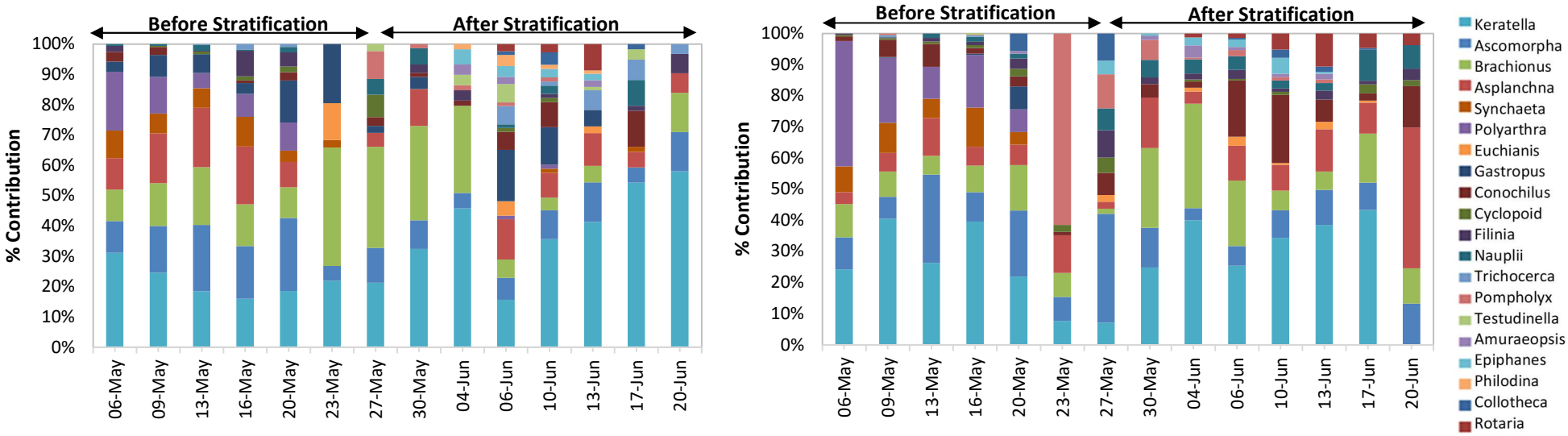

Figure 6.10 (a) Percentage Contribution of Zooplankton counted at Depth 1 (10 cm below the surface) and (b) Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake.

In terms of biomass crustaceans, in general, were the dominant group for both Depth 1 and Depth 2 throughout the sampling period (Figure 6.11a, b). Although, total biomass in pg C ml^{-1} peaked in the time period before stratification at 584 pg C ml^{-1} there was a decline at both depths just prior to stratification. At Depth 1, crustaceans peaked in the days after stratification, while at Depth 2 this peak was not observed until a week after the initial peak seen at Depth 1 (Figure 6.11b). Rotifer biomass was also more abundant at Depth 1 than at Depth 2.

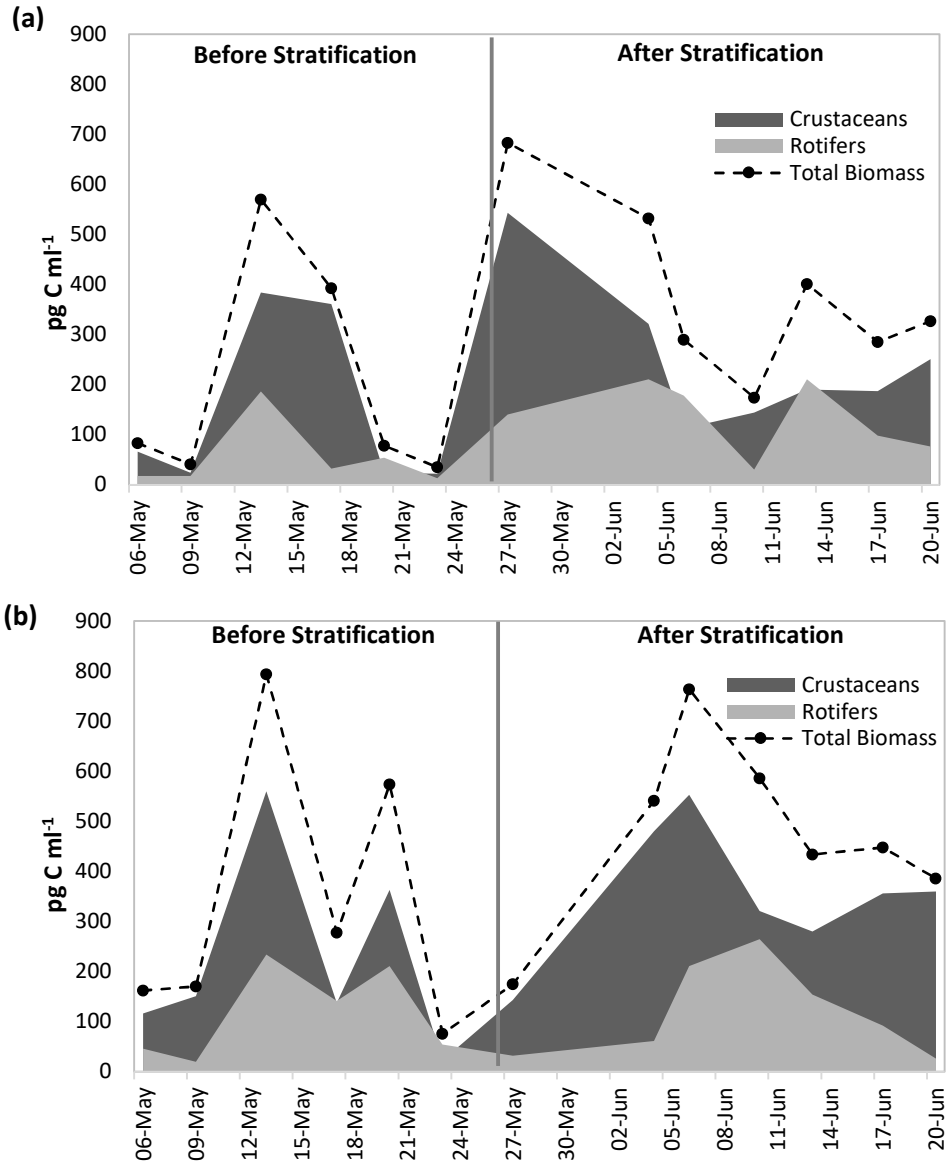

Figure 6.11 (a) Zooplankton biomass (pg C ml^{-1}) counted at Depth 1 (0.1 m below the surface) and **(b)** Depth 2 (Secchi depth), prior to and during the onset of the spring thermal stratification in Milltown Lake.

6.5.7 Drivers of change in phytoplankton group assemblage

All environmental factors considered in the PCA analysis for both Depth 1 and Depth 2 contributed significantly ($p < 0.05$) to explaining variability in the distribution of phytoplankton groups in the weeks leading up to and after thermal stratification in Milltown Lake. The analysis of the phytoplankton group assemblage at Depth 1 (0.1 m below the surface), showed, however, differences in the environmental drivers for each of the six groups (Figure 6.12a). Cyanophytes and Chrysophytes groups were previously reported as being predominantly evident at Depth 1 prior to the lake stratifying on the 26th of May 2013. These had a strong relationship with mean lake thermocline depth (Figure 6.12a) in the PCA analysis. In addition, the Cyanophytes showed a positive relationship with both in-lake NO_3-N concentration and to mean daily stream discharge to the lake. However, the strongest relationship for this group was with in-lake TN, while the Chrysophytes showed a strong relationship with in-lake NH_4-N (Figure 6.12a). After the lake became stratified, the dominant phytoplankton groups at Depth 1 shifted to the Cryptophytes and Euglenophytes (Figure 6.12a). In the PCA analysis, both of these groups showed a dependency on light (i.e. estimated PAR). Additionally, the Cryptophytes had a strong relationship with the lake's stability (S). The Euglenophytes displayed a positive relationship with in-lake dissolved P concentrations (SRP) (Figure 6.12a).

There was a distinctive difference for some phytoplankton groups in the main relationships identified at Depth 2 (Secchi depth) compared to those identified at the near surface depth (Depth 1). For example, the Bacillophytes, which were present dominant during the onset of stratification at Depth 1, were dominant at Depth 2 after stratification (Figure 6.12b). The Cyanophytes which were present prior to stratification at Depth 1 were also present during this time at Depth 2 (Figure 6.12b). However, the Cyanophytes at Depth 2 had a strong relationship with in-lake NH_4-N concentration, as opposed to in-lake TN concentration as found at Depth 1 (Figure 6.12). In addition, the Chlorophytes were also more dominant in the days prior to stratification at Depth 2. They additionally displayed a strong relationship with in-lake NH_4-N

concentration (Figure 6.12b). However, after the lake became stratified at Depth 2, Cryptophytes again showed a strong correlation with lake stability, similar to that identified for Depth 1 (Figure 6.12b). The Bacillophytes at Depth 2 also had a positive relationship to catchment nutrient loading, particularly TN loads (Figure 6.12b). It is important to note that the Bacillophytes at Depth 1 (during stratification) and Depth 2 (post stratification) had an additional pressure from crustacean grazing.

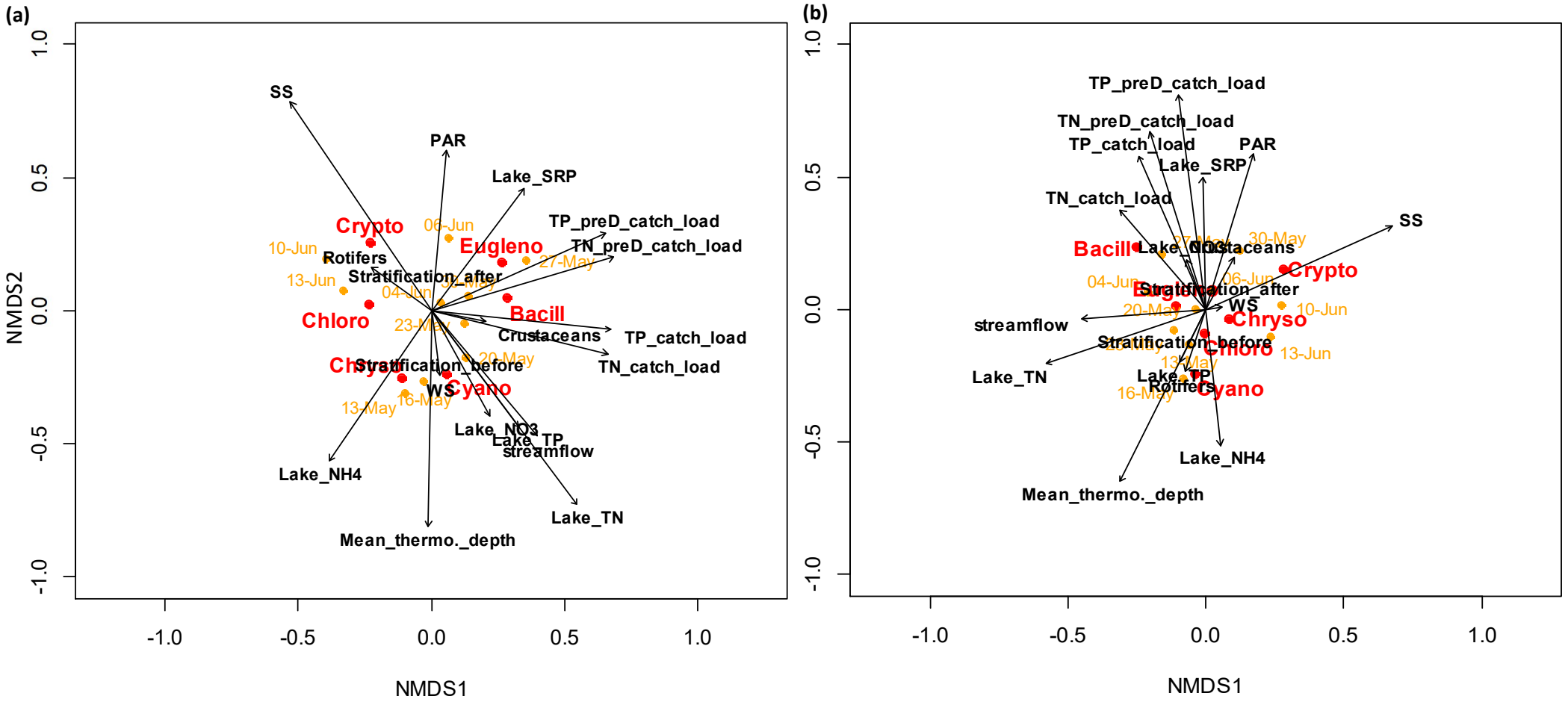

Figure 6.12 Principal Component Analysis (PCA) of individual phytoplankton species (red) and potential drivers (black), before and after thermal stratification (dates in orange) in Milltown Lake at **(a)** Depth 1 and **(b)** Depth 2. WS = windspeed, PAR = photosynthetically active radiation, preD_cath_load = previous day catchment nutrient load, catch_load = catchment nutrient load on the day of sampling, Mean_thermo._depth.= mean lake thermocline depth, SS = Schmidt stability, zooplankton biomass (pg C ml^{-1}).

6.6 Discussion

This chapter focused on the effects of the balance between water column stability, nutrients and grazing in determining plankton abundance and diversity in the lake photic zone. It was informed by the work described in Chapter 5. However, in that year (2012), nutrient levels were consistently high, and the main drivers of phytoplankton biomass (as Chl-*a*) were related to weather and lake physical structure. While in 2013, both external catchment loadings, and internal lake nutrient levels were identified as the main drivers of the phytoplankton community structure. In addition, this study highlighted the differences in phytoplankton abundance at different depths and, therefore, drivers of both phytoplankton community composition and abundance were explored, in particular the possible drivers of any DCM.

Overall, climatic variables such as windspeed and light availability for the sampling period (18th Apr – 20th Jun) in 2013 were similar to those for the same time period in 2012. However, as previously mentioned, 2012 had much higher than average rainfall, which lead to a persistent nutrient loading throughout the summer, leading to high P and N levels in the water column. Nutrient loading from the catchment after rainfall events were also evident in 2013. However, these were much lower than those recorded in 2012. Jennings et al. (2012) describes higher rainfall events leading to increased nutrient loading during spring and early summer as being commonly seen for many western and north western Europe lakes. For Milltown Lake, the rainfall events experienced during spring 2012 also contributed to the periodic breakdown of the lakes thermal structure, with stratification of the lake during this time not exceeding 19 days. It is not known how long the lake stratified for in 2013. However, it was apparent that the lake was more stable when compared to the same sampling period in 2012, as stratification exceeded the 5 week sampling period (~ >35 days). Calmer weather conditions that result in higher lake stability and more frequent algal growth, are generally not expected until the mid to late summer period for western European lakes (Christensen et al., 2007; Sammuelsson,

2010; Jennings et al., 2012). Regardless of not knowing when or what caused the mixing of Milltown Lake in 2013, it is clear that the expected calmer weather conditions, as suggested by Christensen et al. (2007), Sammuelsson (2010) and Jennings et al. (2012), were experienced much earlier in the spring of 2013.

Results presented show clear differences in the drivers (e.g. light versus nutrients) of phytoplankton biomass in sub-surface and potential DCM depths of Milltown Lake during the 2013 sampling campaign. At the sub-surface depth (Depth 1) light and phosphorus availability were the significant drivers of phytoplankton biomass. This was particularly evident for dissolved P, with high concentrations only becoming available in the sub-surface layer in the days prior to and once the lake stratified. While at Depth 2 (potential DCM), nitrogen loading from the Milltown Catchment was identified as the significant driver. In contrast to 2012 where climatic variables and lake physical structure were the main drivers of plankton biomass, the results for the 2013 spring bloom show the importance of nutrient availability in phytoplankton growth.

Martinez et al. (2011) described the occurrence of the phytoplankton spring bloom as a product of sufficient nutrient availability in the upper surface water column coupled with higher irradiance levels, as seen in Milltown Lake in 2013, being the fundamental factors in supporting rapid population growth. The utilisation of light by phytoplankton migrating to the upper surface waters is essential for species survival (Reynolds, 2006). Simmonds et al. (2015) described in their study of lake Õkaro, New Zealand, how sunlight penetrating the surface waters of a lake, inadvertently result in rising water temperatures, a factor which is also essential for phytoplankton growth. However, as described in the updated PEG model, despite the role of temperature being vital in plankton growth, it is light which is considered the dominating factor to trigger the phytoplankton spring bloom (Sommer et al., 2012).

The requirement for adequate levels of PAR was identified as a significant driver of the phytoplankton biomass at the sub-surface depth in Milltown Lake. In addition, in-lake P availability was also found to be significant at this depth for the accumulation of phytoplankton once the lake became stratified. Overall, the relationship with the drivers PAR and P explained 74% of the deviance in Chl-*a,* and therefore, phytoplankton abundance. Phosphorus concentrations in the lake at the start of the sampling campaign were again high throughout the water column, similar to the preceding year. This did not coincide with a peak in P loading from the catchment. Phosphorus that has accumulated within the lakes sediment under anoxic conditions can be re-introduced to the surface waters through deep winter mixing (Wang et al., 2008; Hupfer and Lewandowski, 2008; Martinez et al., 2011). However, in the days prior to the lake stratifying, high concentrations of dissolved P became evident only in the surface mixed layer of Milltown Lake, thus suggesting that the sediment was not a source P at this time. This peak in P coincided with high P loadings from the catchment.

Catchment nutrients were, again, found to influence plankton growth at Depth 2. Dominance shifted from catchment P concentrations driving plankton growth in the sub-surface depth to catchment N concentrations stimulating plankton growth at Depth 2 (32% deviance explained). Continuous high N concentrations from the lake's inflow in the two weeks prior to the lake stratifying on the 26th of May, became available throughout the lakes profile. This highlights how nutrient loadings from the catchment during critical time windows can have significant implications for phytoplankton biomass, particularly in the lakes photic zone.

As mentioned previously, the PEG model conceptualises the seasonal dynamics of plankton growth (Bentrup et al., 2016). The model hypothesises that physical controls are mainly attributed to plankton growth at the start and end of the plankton growing season and is not a contributing factor throughout the season (Bentrup et al., 2016). The first step of the model

highlights how the availability of nutrients and light towards the end of the winter period contribute to a small crop of fast growing algae such as Cryptophytes (Sommer et al., 1986; 2012). This only became evident in the sub-surface depth of Milltown Lake where the tail end of a Cryptophyte peak was observed. This peak coincided with high levels of SRP within the sub-surface depth. Sommer et al. (1986) notes in their paper that Cryptophytes are capable of depleting this form of P to near undetectable levels. A depletion in SRP concentrations was noted in the sub-surface waters of Milltown Lake after the peak in Cryptophytes, however, levels were still detectable.

At the same time as the Cryptophytes peaked in the sub-surface of Milltown Lake a peak in Cyanophytes (*Zygenema* spp.) was recorded at Depth 2. It appears that as the days progressed, the Cyanophytes (*Zygenema* spp.) migrated up to the sub-surface depth, with biomass at Depth 2 decreasing while at the sub-surface an increase in biomass was recorded. Cyanobacteria have the ability to form motile filaments, called hormogonia, which can travel away from the main biomass to form new colonies elsewhere (Reynolds, 2006). In addition, the PCA analysis carried out in this study highlighted the strong dependency this species has with in-lake N. Cyanobacteria are said to favour elevated NO_3 and NH_4 concentrations within a lake's ecosystem (Beversdorf et al., 2013; Paerl and Otten, 2013). Jackson et al. (2016) reported similar dominance of Cyanophytes prior to stratification in their study of several lakes in the USA and China. They demonstrated how Cyanophyte dominance correlated significantly with elevated NO_3 and NH_4 concentrations in the lake. Jackson et al. (2016) attributed this association to the ideal ratio of NO_3 and NH_4 concentrations in the water column. There was short period after the Cyanophytes at Depth 2 declined, where a Raphidophytes taxa (*Gonyostomum* sp.) was recorded. The numbers of this taxa were low (only two individuals were observed). This species is known as a nuisance alga mainly due to their size 36 – 92 µm

and issues with drinking water taste and odour episodes. (Johansson et al. 2013; Watson et al., 2015).

The PEG model surmises that once the fast growing algae have developed, the next stage involves grazing by herbivorous zooplanktonic species, whose population increase is due to the availability of food (Sommer et al 1986; 2012). Within Milltown Lake, both crustaceans and rotifers increased in response to the availability of food, with lag peaks for both the sub-surface and Depth 2 being observed following the Cryptophytes and Cyanophytes blooms. Following, this initial grazing by the zooplankton, new planktonic herbivores with short generation times begin to increase their population (Sommer 1986; 2012; Davis et al., 2012; Ger et al., 2016).

Diatoms have been recognised as the most opportunistic of the phytoplankton species as far as taking advantage of nutrient availability is concerned (Olli et al., 1996; Çelik and Ongun, 2007; Frasquet et al., 2012) and are said to prefer well mixed water columns where turbulence keeps them in the photic layer (Reynolds, 2006; Watson et al., 2015). In the days prior to stratification in Milltown Lake, turbulence due to increased wind speed was evident in this study, which contributed to a dominance shift from the Cyanophytes to the Bacillophytes (*Astrionella sp, Cyclotella sp*) in the sub-surface depth. The Bacillophytes bloom at Depth 1 was short lived, most likely due to the decline in windspeed, increased water column stability, and the high settling rates of diatoms (Reynolds, 2006). With a decline in windspeed noted during this time, it is probable that the diatoms (due to them being non-motile) settled down to Depth 2 just as the lake began to stratify (Monero-Osten et al., 2009). Furthermore, a peak in crustaceans was also observed during this period at the sub-surface depth, which may have provided additional pressure on the decline in population. The PCA analysis of the phytoplankton assemblage indicated catchment P to be the limiting factor at Depth 1, while catchment N loading was the limiting factors for the Bacillophytes at Depth 2. It is generally reported that diatom blooms in

freshwater lakes are commonly associated with high in-lake P levels (King et al., 2000; Bradshaw et al., 2002; Ramstack et al., 2003; Wang et al., 2012; Watson et al., 2015), which was evident in the sub-surface depth. However, a study by Scotese (2008) indicated that both P any N can be important component in limiting the growth of diatom species. This became apparent in Milltown Lake, as windspeed decreased the adaptability of the non-grazed, non-motile diatom species allowed them to adjust from the P rich environment found in the sub-surface to the N rich environment found at Depth 2.

As a result of diatoms migrating to the lower depth, the Bacillophyte bloom at Depth 2 was not evident until approximately a week after the initial bloom was seen in the sub-surface depth. It is apparent that the diatoms at Depth 2 were also grazed by crustaceans as a lag peak in the zooplankton productivity was also observed for this depth. Sommer et al. (1986; 2012) outlines in step 5 of the PEG model that, as a consequence of zooplankton grazing, phytoplankton species decrease rapidly to very low levels, creating a clear water phase. This becomes apparent in Depth 2 after the diatom bloom, because an increase in alternate diatom population is not seen before the end of the sampling campaign. In addition, wind speed during this time decreased, which could also contribute to the decline in the diatom community at Depth 2. Monero-Osten (2009) studied the impact of short-term wind induced mixing and found a decline in positively buoyant diatoms in the epilimnion became apparent during periods of low wind speeds. However, this is not the case for Depth 1, because a further population increase in Cryptophytes is seen at the same time as the Bacillophytes bloomed at Depth 2.

After the depletion of the Bacillophytes in the sub-surface depth and stratification has been established in the lake, both the Cryptophytes (*Cryptomonas sp, Rhodomonas sp*) and Euglenophytes (*Euglena* spp. and *Trachelomonas volvocina*) became the dominant groups at the sub-surface depth. Similarly, Harris et al. (2016) reported a spring bloom of Cryptophytes

during the stratification of four reservoirs in the Midwestern United States. Their study attributed this to increased lake temperature and stability all of which are favoured by the Cryptophyte taxa. Principal component analysis for this study also identified this dependency with lake stability. Regarding the dominance of Euglenophytes, various studies which observed changes in group assemblage during lake stratification have identified high nutrient levels and decreasing turbulence as their main drivers (Olli et al., 1996; Çelik and Ongun, 2007; Frasquet et al., 2012). Euglenophytes have been identified as suitably adjusted to small lakes (Zakrys et al., 2004), like Milltown Lake. The PCA analysis at the sub-surface depth of Milltown Lake identified both in-lake N and lake stability as the main drivers of the Euglenophytes assemblage, similar to studies by Çelik and Ongun (2007) and Frasquet et al. (2012). However, in addition to stability and nutrient availability, their analysis also indicated that the breakdown of the Cryptophyte taxa was due to the equal grazing pressures of both the crustaceans and rotifers.

The findings in this chapter demonstrated that different factors are playing an important role in determining the assemblage of diverse phytoplankton groups at the different depths within Milltown Lake. Reynolds (2006) describes how temperature and light are the main variables triggering a spring bloom formation. Further work by Sommer et al. (2015) argues that, although temperature plays a vital role in the formation of the spring bloom, it is in fact light that triggers blooms. This can be seen in the GAM analysis for Milltown Lake, which demonstrates how light and nutrients were the main driver of the spring bloom in 2013. Regarding dominant species composition within a spring bloom, Sommer et al. (2015) describes how diatoms are commonly found in eutrophic systems during the spring formation. This theory can also be applicable to Milltown Lake, as the dominant taxa during the formation of the spring bloom were the diatoms (*Asterionella* sp. and *Cyclotella* sp.) at both the sub-surface and the lower depth.

6.7 Conclusion

This chapter has improved understanding of how phytoplankton taxa, and therefore phytoplankton biomass, respond to the combination of water column stability, nutrients and grazing at different depths within the photic zone. The chapter built on the findings of Chapter 5, which highlighted the role of climatic factors in influencing phytoplankton biomass. That year (2012), however, was usually wet and therefore, there was a high nutrient loading to Milltown Lake throughout that summer. This additional study, in 2013, has demonstrated that the drivers of phytoplankton biomass can change on a year-to-year basis as, in 2013, both external catchment loading and internal lake nutrient levels were the main drivers of the phytoplankton community, with distinct changes also occurring at the time of stratification. These insights are important in highlighting the complexity of the controls on a lake's community structure and illustrating that both weather-related changes in stability, and nutrient loading and availability, affect the Chl-*a* concentration in a lake. In particular, this chapter has highlighted how long-term monitoring programmes need to be adapted to gain a true understanding of the different processes occurring within a given lake so that these processes can be taken into account during lake management activities.

Chapter 7: Final Discussion

7.1 General overview

It has long been recognised that nutrient enrichment of freshwater ecosystems plays a key role in the amplification of algal blooms (Paerl and Fulton, 2006; James et al., 2009; Cai et al., 2012). In Ireland, nutrient enrichment of freshwaters, particularly from agricultural sources, has been highlighted as an important environmental issue (Kelly, 2009; Bradley et al., 2015; Deakin et al., 2016). Agriculture in the ROI accounts for 67% of the total land area (CSO, 2015), which is linked through an intricate network of lakes and rivers that flow through the landscape. It is currently estimated that 64% of the rivers and lakes within the ROI are currently *At Risk* of not meeting their environmental objective of good ecological status (Department of Housing, Planning, Community and Local Government, 2018). Of the estimated 64% of river and lakes failing to meet the WFD objectives, 53% are suspected to be as a consequence of agricultural sources of pollution (Bradley et al., 2015; Deakin et al., 2016).

In recent years, it is becoming more apparent that climate change, either directly or indirectly, may cause qualitative changes in the dynamics of the phytoplankton communities within lakes (Stella et al., 2007; Jackson et al., 2007; Adrian et al., 2010; Sommer et al., 2012; de Senerpont Domis et al., 2013; May and Spears, 2015; Havens et al., 2016; Paerl et al., 2016; Dalton et al., 2016). Factors such as rising air temperatures have been reported to encourage undesirable plankton species such as cyanobacterial species (O'Neil et al., 2012; Deng et al., 2014; Rigosi et al., 2014; Woolway et al., 2019). However, other environmental changes including rising water temperatures and increased rainfall leading to higher nutrient runoff from the surrounding catchments are also increasing eutrophic conditions in freshwater ecosystems (Jeppesen et al, 2009; Moss et al., 2010; Deng et al., 2014). The current study aimed to explore the relative effects of nutrient export from a rural catchment and of local meteorological conditions as

drivers of change in phytoplankton biomass in a small eutrophic lake and, in turn, provide valuable information that can be used to inform the future management of these systems .

7.2 Overview of the trophic status of Milltown Lake and links to catchment nutrient export

Analysis of the water quality in Milltown Lake indicated that the lake was classified as strongly to highly eutrophic during the course of this study. The maximum Chl-*a* concentration recorded in 2012 was 44.5 μg L^{-1} and 2013 was 65.0 μg L^{-1} . Milltown Lake's classification was based on the modified O.E.C.D scheme, which determines status from annual maximum Chl-*a* concentration (O.E.C.D, 1982; EPA, 2015). Previous work carried out by Carson et al. (2015), which included water sampling over two years (2007-2008) and a paleolimnological investigation, concluded that the lake had fluctuated between mesotrophic and eutrophic conditions in the recent past. Furthermore, from the analysis of four years of high frequency temperature profile data as part of the current study, the lake was confirmed to be slightly polymictic in nature. The data presented for 2012-2013 also indicated that it experienced periods of hypolimnetic oxygen depletion during the summer months. Similar findings were reported by Carson et al. (2015) for Milltown Lake during 2007-2008 based on temperature and DO profiles taken at weekly intervals.

It is of note that, five years on from the Carson et al. (2015) study, Milltown Lake has not shown any improvement in classification. In fact, the results presented in this thesis may indicate further deterioration, as the lake was classified as strongly to highly eutrophic in 2012 and 2013. At the very least, the status had not improved. This lack of any improvement was despite the implementation of fencing on one third of the catchment streams as described and investigated in Chapter 4. The paleolimnological study carried out by Carson et al. (2015) concluded that agricultural practices in the Milltown catchment had been impacting the lake since the 1970s

and thus were the leading contributors to nutrient loading. Those results led to the installation of cattle exclusion fencing in 2008, with a 1.5 m vegetative buffer along the western most tributary to support a reduction in nutrient pollution from cattle-based agriculture in the Milltown Catchment.

The current study investigated the impact of this exclusion fencing by comparing the nutrient concentrations from a fenced stream reach with those of an unfenced stream reach that had similar land management practices. It was found that the annual estimated TP and TN export rates from the catchment area were reduced in the fenced tributary (0.57 kg TP ha^{-1} yr^{-1} and 5.99 kg TN ha^{-1} yr^{-1}) compared to the unfenced tributary (0.77 kg TP ha^{-1} yr^{-1} and 7.24 kg TN ha^{-1} yr^{-1}). However, the results also indicated that the exclusion fencing was only effective during the grazing season, when cattle were in the fields, nutrient uptake by plants would be at its highest, and buffer vegetation biomass would be at its greatest. Similar findings in relation to seasonality in the mitigation potential of fencing and associated vegetation have been reported in a number of other studies. Dorioz et al. (2006), Stoate et al. (2009), Roberts et al. (2012) and McConnell et al. (2013) all found that bioavailable P and N uptake by the vegetation within the buffer were at their highest during the growing season. In addition, the capacity of the vegetative buffer to trap particulate nutrients were higher at the time of year when the vegetation was denser (Dorioz et al. 2006; McConnell et al. 2013).

In contrast, the findings from the current study also indicated that streamside exclusion fencing was not effective in the management of TP in the late winter and early spring when the vegetation cover in the buffer zone had died back. A similar result was reported by Stoate et al. (2009) and Hoffmann et al. (2009), who also concluded from their work that grassy buffer strips were ineffective in retaining P during early spring, particularly after heavy rainfall events, when vegetation was underdeveloped. This time period will also coincide with the time when slurry

spreading resumes in Ireland following winter, which would be after the 31st of January in this catchment under the 2017 Good Agricultural Practice for the Protection of Waters Regulations (S.I. No 605 of 2017). In the current study, TP loads from the fenced catchment exceeded those from the unfenced catchment at this time of year. It could be argued that the overall effect of this was that fencing delayed the export of P to the lake until a time of the year when its impact may actually be greater, i.e. in the spring prior to the main period of algal growth in the lake.

Despite this possible spring effect, the study of the in-lake responses indicated that nutrient control using exclusion fencing is important during the most critical time window for algal blooms, i.e. early to late summer. However, it should be noted that the retention time of Milltown lake is short (25 days), and therefore, this lake will have a rapid response time to increased or decreased catchment nutrient export. The effect of increased TP loading during the early spring in lakes with a longer response time would likely be prolonged into the main algal growing season. Similar cattle exclusion measures to those implemented in Milltown Lake have recently been included in the 2017 GAP Regulations. These stated that livestock are not permitted to drink directly from waterbodies, and that river and streams should be fenced off with a 1.5 m buffer from the 1st of January 2021 (S.I. No. 605/2017). Fencing of the remaining tributaries as a catchment nutrient reduction measure in the Milltown Lake Catchment could further decrease loading to Milltown Lake during the summer but could also increase TP loading during the early spring, and therefore, may not improve the trophic status of the lake.

7.3 Drivers of phytoplankton biomass within small lakes

The results presented in this thesis also showed that Milltown Lake was highly responsive to meteorological factors, which affected the lake thermal regime during the spring and early summer stratification and the export of nutrients to the lake. Ireland has a milder, more moderate oceanic climate, with high precipitation rates and variable wind speeds (Keane, 1986), than

many regions of a similar latitude. The future climate projections for Ireland include rising air temperatures and increased rainfall events, resulting in wetter winters and drier summers respectively (Sweeney, 2008; Gleeson et al., 2013; Matthews et al., 2016). It is of note that the largest range in air temperature and lowest recorded rainfall was seen for the Milltown Catchment in the summer of 2010 compared to the subsequent years studied in this research (2010 – 2013). In response to this, Milltown Lake stratified for longer periods in 2010 than in the two years when the more detailed lake study was conducted (2012 and 2013), with much stronger buoyancy frequency, and a more consistent stable thermocline. Such warmer summers are projected to occur more frequently in Ireland in the future (Gleeson et al., 2013; Matthews et al. 2016) and will likely result in longer and more intense stratification in the lake. However, future projections also include wetter periods in the spring and early summers (Sweeney, 2008; Jennings et al., 2012; Gleeson et al., 2013; Matthews et al., 2016; Coffey et al., 2016). In 2012, higher rainfall over the summer also contributed to higher TP and TN export from the surrounding catchment, and separately contributed to the initial breakdown of thermal stratification. Jennings et al. (2012) noted that similar intense precipitation events may result in physical disturbances of the water column and, in addition, can be accompanied by pulses of nutrient exported from the surrounding catchment to the lake. The results of this study in the Milltown Catchment illustrated the effect of particularly heavy rainfall events on the nutrient levels in 2012 to a lake that was already affected by high nutrient loading (Jordan et al., 2005; Macintosh et al., 2011). However, interestingly, the lake was not nutrient limited in 2012 and, therefore, lake phytoplankton was even more sensitive to climatic factors than in 2013.

When both study years (2012 and 2013) are taken together, it was clear that both climatic factors and nutrient availability played a significant role in driving in-lake Chl-*a* levels, but that this is very much dependent on weather conditions in a given year. In spring/summer 2012, the main drivers of Chl-*a* biomass were climatic factors, although these affected the lake differently over

the depth profile. The upper 2 m were influenced by mixing forces from wind speed and stream discharge, whereas the lower depths were influenced by light availability and NH_4 release under anoxic conditions from the lake sediment. However, in spring 2013, PAR was the only significant climatic factor of the variables assessed that influenced Chl-*a* concentrations, with nutrients, especially N, affecting the phytoplankton biomass.

It is worth noting that, even though different climatic variables were important drivers of phytoplankton biomass, in 2012 and 2013 the spring bloom appeared to be triggered by light (i.e. PAR) from the upper surface to 2 m depth. This is in line with the updated PEG model of Sommer et al. (2012), which assumes that, although temperature plays a vital role in spring bloom formation, it is light that triggers spring bloom formation. Regardless, studying the responses in the two contrasting years has highlighted the complexity of the Milltown Lake ecosystem and how rapidly it changes and responds to constantly changing weather patterns and nutrient inputs.

7.4 Implications of management

Limnological investigations increase our understanding of lake dynamics and help to explain changes in water quality over the annual cycle. However, as this study has shown, it is the larger catchment-scale that needs to be studied, not only the internal functioning of the lake, or indeed the catchment, as single entities. This study has highlighted the complexity of lake ecosystems and how readily they respond to their changing environment. One of the suggestions made by Carson et al. (2015) for the Milltown catchment was to reduce soil and nutrient transfers at their source, which the authors concluded, would be the only sustainable way to improve water quality. However, Deakin et al. (2016), showed that, to reduce nutrient transfer, the pathways of these nutrients need to be targeted from source to receptor, rather than simply the source alone, and that mitigation measures need to be implemented on a case by case basis rather than

on a national scale. This study has shown that measures such as streamside fencing, which is a remedial measure commonly used for the reduction of soil and nutrient transfer, is not always effective. To employ streamside fencing effectively within a catchment, additional management strategies such as farm to field nutrient management programmes also need to be operated concurrently. In addition, the surrounding landscape of a given catchment would need to be assessed to see whether fencing would be a viable option. Milltown Lake Catchment is situated within a rural agricultural setting in a drumlin landscape of Ireland and the surrounding topography often does not lend itself well to nutrient reduction though the use of vegetative buffers, especially during hydrologically active periods and during times of high rainfall when the floodplain may exceed the buffer width.

Carson et al. (2015) suggested further that nutrient loadings from the surrounding catchment, either from agricultural sources or domestic wastewater treatment systems, were the leading factors contributing to Milltown Lake's overall load. Studies by McCarthy et al. (2012) and Rafferty (2015) also showed that high nutrient concentrations from the unsewered rural population in the catchment were likely to have impacts on the water quality, but these were found to be much lower than those from agricultural sources. Within Ireland, regulations have been put in place that impose time constraints on the spreading of inorganic and organic fertiliser on land and a limit on the amount of livestock manure that can be spread on the land (S.I. No. 605 of 2017; Buckley, 2012). These regulations will be of benefit to catchment load nutrient management. However, when external loads to rivers and lakes are reduced, it is likely that legacy issues will mask the immediate impacts of these contemporary conservation measures (Meals et al., 2010; Spears et al., 2012). These legacy issues, associated with the remobilisations and recycling of P in the catchment, may continue to contribute to the overall nutrient load for years, decades, or even centuries to come (McDowell et al., 2002; Kleinman et al., 2011; Sharpley et al., 2013).

Furthermore, the current study showed that, not only are external nutrient sources from the catchment playing a role in maintaining Milltown Lake's eutrophic status, but internal nutrients from sediment release may also have an influence. The factors that are mainly influencing this re-suspension are periods of anoxia within the hypolimnic layer. While the negative impacts associated with this phenomenon can potentially be addressed with engineering solutions through the oxygenation of hypolimnetic waters during stratification (Beutel, 2006) or chemically increasing the P binding capacity of the sediment (Wauer et al., 2005), such an approach does not offer long term sustainable solutions to deterioration in water quality (Lürling et al., 2016; Huser et al., 2016) . In addition, this study found that in Milltown Lake P concentration was not the only nutrient leaching from the bed sediment but also NH_4, which played a key role in enhancing phytoplankton biomass within the lake.

Finally, while it is important to have a good understanding of how a lake responds to external and internal nutrient loads, this study has also highlighted the potential sensitivity of a lake to meteorological influences. Forecasting a lake's response to future climate change scenarios can be challenging, especially on a local to regional scale (Paerl et al., 2016). However, as this study has demonstrated, future lake management strategies need to not only consider the role of nutrient loads but also the potential influence of climate change when developing future measures, a factor that is normally not considered.

7.5 Overall conclusion

Previous work in the Milltown catchment highlighted the impact of external nutrient loading on Milltown Lake's ecosystem, with losses from agriculture being one of the main drivers. The evidence provided by this study has confirmed that Milltown Lake is still heavily impacted by external nutrient loads. However, the impact of internal lake nutrient re-suspension and climatic factors also play a role in the lake's ecology. It is apparent that agriculture is a significant

pressure in the overall contribution of nutrients to Milltown Lake. However, for water quality in Milltown Lake to improve, management strategies need to be considered for the ecosystem science of the entire catchment including the lake itself. It is important to continuously strive for improvements, particularly as the lake is used as a drinking water source, fishing amenity and as a habitat for a variety of different plant and animal species.

In addition, this study has demonstrated that streamside fencing as an exclusion measure can be beneficial within the catchment, particularly during the summer months which is a critical time period for the lake. However, this measure can be costly. Therefore, before installing fencing it is important to consider both the positive and negative implications and weighing up the cost benefit, before considered it a viable solution. Furthermore, this thesis has demonstrated the complexity involved for both stakeholders and policy makers in implementing a universal strategy that will reduce nutrient pollution on a national scale. Each catchment and lake respond differently to different management strategies. Also, each year, different climatic variables influence different freshwater ecosystems in different ways.

Finally, this thesis has demonstrated how developing a good database which provides an overall picture of the catchments behaviour with respect to nutrient loss and its response to local climatic stresses is important. However, it will be important that the information can be of benefit to the stakeholders within the community (i.e. the local community, GWS, farmers, angling groups etc.), in order for them to build on this knowledge. It may, therefore, be feasible based on these finding to encourage a Citizen Science based approach in this catchment, at a much reduced sampling scale. This will still allow for crucial information to be gathered, and allow for further management strategies to be developed, which will further aid water quality improvement. The findings of this study and through community engagement, the information obtained will not only be beneficial to catchments with similar river lake continuums, but also

to neighbouring communities through the encouragement of local stakeholder engagement. This approach can give the local community a sense of ownership and connection with their local waterbodies.

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